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THE REFRACTION OF GASES AT DIFFERENT TEMPERATURES AND PRESSURES.

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Historical.

THE greater part of the early investigations on the subject of the refraction of gases was done with one of two aims in view: (1) the determination of the constants necessary for the correction of astronomical observations, and (2) the experimental verification of the constancy of the relation $(n - 1)/\rho = \text{constant}$, which expression is derived from theoretical considerations in the emission theory.

In general, two methods have been employed in the investigations of the subject, namely: the prism method and the interference method. Much of the early work was done by the prism method. Dulong,[1] for instance, in 1826 used a hollow prism made from a metal tube, the ends of the tube being cut at an angle to its length and closed by means of plates of glass. He used a constant deviation, that is, ran the gas into the prism until the deviation in each case was the same. Arago in his earlier work used the prism. Gladstone and Dale[2] used the prism method in the work in which they established the constancy of the relation since known under their name.

Probably the first to apply the method of interference to the problem was Arago in 1821.

Since that time various modifications of the method have been used, probably the best known of which is that due to Jamin.[3] Mascart[4]

[1] Annales de chim. et de phys., 2 ser., t. XXXI., p. 154, 1826.

[2] Phil. Trans., p. 887, 1858; Phil. Trans., 153, 1863, pp. 317–343.

[3] Ann. de chim. et de phys., t. LII., p. 1858; t. LXI., p. 385, 1861; Comp. Rend., 1856, p. 1191; Vol. 45, 1857, p. 1892.

[4] Ann. sc. de l'Ecole Normale sup., 2 ser., t. VI., p. 9, 1877; Comp. Rend., Vol. 78, pp. 617, 679, 801, 1874; Vol. 86, pp. 321, 1182, 1878.

working with the same apparatus made some refinements and rediscussed much of the earlier work of Jamin, showing that the observations could be more nearly expressed by the relation $(n - 1)/\rho = \text{const.}$ than by the equation $(n^2 - 1)/\rho = \text{const.}$ used by Jamin.

Perreau[1] made some further modifications in the apparatus and studied the refraction and dispersion of hydrogen, carbon monoxide, and carbon dioxide, at room temperature, and pressures (differentially) to about five atmospheres.

Kayser and Runge[2] have used the prism more recently in connection with the grating.

Chappuis and Riviere[3] used a modification of Jamin's method, studying air, carbon dioxide, and cyanogen at ordinary temperature and at pressures up to 20 atmospheres. These gases were chosen because they differ widely in their densities and other physical properties. For air, the densities were computed by means of Van der Waal's equation and the constancy of the equation $(n - 1)/\rho = \text{const.}$ was found to hold within experimental errors.

For carbon dioxide, a formula from Clausius was used in computing the densities, the coefficients proposed by Sarrau being adopted. In the case of this gas a linear relation was found also.

Benoit,[4] in the course of an investigation on the comparisons of meter bars by means of the Fizeau dilatometer, had occasion to make correction for the refraction of the air. He tested the validity of the relation

$$n_1 - 1 = \frac{n_0 - 1}{760}(1 + 0.00367t)$$

by the use of his apparatus, making observations in vacuo and in air at a pressure of one atmosphere. His observations extended over a range of temperature from 0° to 80°. The results obtained verified the correctness of the expression for the pressure and temperatures used.

Apparently the only work so far published, in which the observations

[1] Ann. chim. et de phys., (7) 7, p. 289, 1896.

[2] Ann. der Phys., Vol. 20, p. 293, 1893; Abh. der Berl. Akad., 1893.

[3] Ann. de chim. et de phys., 6 ser., Vol. 14, p. 5, 1888. (For further modifications of Jamin's principles and applications of the apparatus see: Traver's Study of Gases, Ch. XXI.; Burton, W., Roy. Soc., Proc., 80, 1908, p. 390; Magri, L., Phys. Zeitschr., *6*, 1905, p. 629; Rayleigh, Nature, 81, 1909, p. 5191; various communications to Roy. Soc., Proc. and Phil. Trans., beginning in 1904, by Cuthbertson, C.)

[4] Jour. de Phys., 2 ser., 8, p. 451, 1889. (For other work on refractivity see: Nagaoka, H., "Relation between Index of Refraction and Density," Math. and Phys. Soc., Tokyo, 2, 19, pp. 293, 1905; Rentschler, H. C., "New Method of Measuring the Index of Refraction of a Gas for Different Light-waves," Astro. Phys. Jour., 28, p. 345, 1908; Siertsema, L. H. and de Haas, M., "Refractive Indices of Gases under High Pressures," Konink. Akad. Wetensch. Ams., Proc., *14*, p. 592, 1912.

were extended to low temperatures is that of Scheel.[1] Observations were made at liquid air temperatures on atmospheric air, nitrogen, and hydrogen, at a pressure of one atmosphere, that is, readings were made in vacuo and at a pressure of one atmosphere. Assuming the correctness of the expression $(n - 1)/\rho$ = constant, Scheel deduces the values of the densities of the gases at liquid air temperatures from the refractive indices and compares the results with those obtained by other methods, and with the values computed from the gas laws. His conclusions were, that within the limits of accuracy of observation of his experiments, the constancy of the relation is established.

Other expressions have been derived in the attempt to represent more closely the relation between the refractive indices and the density, the most notable of which is probably that arrived at independently by Lorentz[2] and Lorenz[3] and known as the Lorentz-Lorenz formula. By a simple approximation it passes into the Gladstone and Dale formula, and on the whole it seems to be an open question whether this more complex formula represents the facts more closely than the simpler expression of Gladstone and Dale.

It appears that the method of arriving at the proper value of the densities may be a matter of greater importance than the small differences in these formulæ. Including the usual method of taking the density as directly proportional to the pressure we have already noted three methods of deducing the densities. Whatever question may remain as to the superiority of this expression or that, it is evident that the relation between the refractive indices and pressure is not in all cases a linear one.

Method and Apparatus.

In the experiments to be described in this paper the interference method was used, and the change ensuing in the optical path of light traversing twice, the distance between two reflecting surfaces upon admitting a gas to the space between the surfaces was determined. If one represents by k the total shift of interference bands of wave-length λ, and by n the index of refraction of the gas, then one has the relation

$$n - 1 = k\lambda/2d,$$

[1] "Bestimmung der Brechungsexponenten von Gasen bei Zimmertemperature und bei der Temperature der flussigen Luft," Verhand. der Deutsch. Phys. Gesell., IX. Jahrg., Nr. 1, 1907.

[2] Wied. Ann., *9*, 642, 1880; *11*, 77, 1880.

[3] Jour. de Phys., 447, 1885. (For other expressions connecting refractive indices and density see: Edwards, Amer. Chem. Jour., *16*, 625, 1894; *17*, 473, 1895; Nagaoka, Math. and Phys. Soc., Tokyo, *2*, 19, 293, 1905. For further concerning Gladstone and Dale's formula see: Landolt, Lieb. Ann., Suppl., *4*, 1, 1865; Sutherland, Phil. Mag., *27*, 141, 1889.)

where d is the distance in cm. between the surfaces. At a given temperature, since d is constant and k depends upon the pressure, it may be noted that values of n are obtained for corresponding values of the pressure.

The general plan of the apparatus used and also many of the details of manipulation have been described in previous articles in this journal[1] on expansion work at low temperatures. Many modifications in the apparatus were required however, and after considerable preliminary work, testing different schemes in the attempt to obtain a vessel suitable for containing the interference apparatus and which would hold at liquid air temperatures a vacuum or a gas under considerable pressure, the form of the apparatus described below was finally used.

The interference apparatus consisted of two plates, 18 mm. in diameter; one, G_B (Fig. 1) was of black astronomical glass with one face plane and polished, the other, G_0, of optical glass, both faces being plane and polished and inclined at an angle of a few minutes to each other. A hollow cylinder of quartz Q about 15 mm. in length separated the plates, thus giving an optical path of some 30 mm. with a vacuum or a slightly longer path when the gas was admitted. The adjustment of these parts in the steel chamber as first used was as follows: a brass disk of diameter slightly less than the inside diameter of the chamber had one surface cut out, leaving a thin rim around the edge within which the black plate would rest. To the under side of the disk were attached three small spiral springs of such length that when the two plates and quartz cylinder were in place, the upper surface of the top plate projected slightly above the top of the chamber. Upon inserting the plate glass cover disk, the springs were compressed and the parts were thus held snugly against each other, the upper surface of the optical glass being in contact with the lower surface of the cover disk. With this arrangement, however, the fringe system was altered by tightening one or another of the screws by which the chamber was held in place, and upon cooling to liquid air temperature the fringes became very much distorted. It was thus evident that the optical system must be kept free from contact with the side of the chamber, at least toward the lower end. In order to accomplish this, the optical glass plate G_0 was attached to the cover disk G_P by Canada balsam being placed concentrically with it. A hollow brass cylinder C of diameter slightly greater than that of the disk and having a very thin wall was made, and the springs s, s for holding the quartz cylinder and black glass in place were mounted on the lower edge of this brass shell. Also to its lower end were soldered the three phosphor bronze springs S to rest on the bottom of the chamber and thus keep

[1] Vol. 20, p. 38, 1905; Vol. 25, p. 58, 1907, and references in these articles.

the top of the shell in contact with the plate cover disk. Since the optical glass G was fixed in place, it held the other parts in the center of the chamber by means of the brass shell. In this manner no contact was made with the outside chamber except through the springs, and the slight motion of the bottom of the chamber was not sufficient to cause a distortion of the fringe system through them.

But one serious trouble arose with this arrangement; at liquid air temperature the Canada balsam underwent some peculiar changes, becoming almost opaque at one temperature, or at one stage of the transitions. To remedy this, it was removed from the plates and three drops of solder placed on the outside of the brass shell very near the top to keep the optical system concentric. This arrangement proved satisfactory.

The chamber for containing the gas and interference apparatus was made from a piece of seamless steel tubing 2.2 cm. in diameter, and about 4 cm. long. Into one end of this was brazed a disk cut from a piece of strap steel, thus closing the end. Into the other end was ground a disk of plate glass G_P, the finishing being done with a very fine grade of carborundum powder. To the side of the tube was attached a piece of brass tubing for exhausting and admitting the gas. The chamber was mounted at the end of a quartz tube 18 mm. inside diameter and 23 mm. outside diameter and about 40 cm. long.

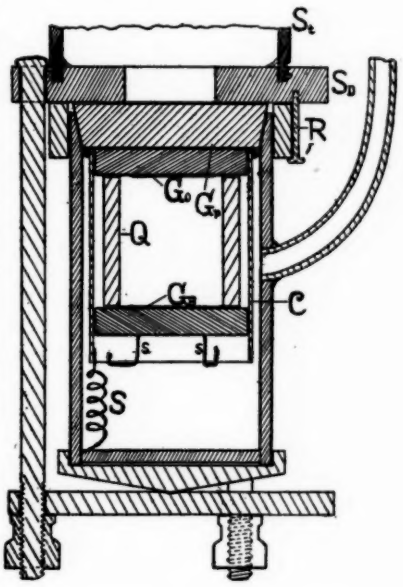

Fig. 1.

Fig. 1 is a drawing of the vertical cross section of the chamber. It shows also the plan used in attaching it to the quartz tube. A short piece of steel tubing, S_t, of diameter such that it fitted closely over the end of the quartz tube was screwed into and soldered to a steel disk S_D. The steel tube S_t was attached to the quartz tube by means of plaster of Paris.

The steel disk S_D had an opening in its center 1 cm. in diameter for admitting the light to the chamber. The lower side of the disk was ground plane and the plate cover glass G_P rested against it with stopcock

grease between the surfaces. In this manner the lower end of the tube was made airtight, though it was not exhausted. In order that the chamber take a position concentric with the opening in the steel disk, a brass ring R was attached to the former.

The upper end of the quartz tube was set by plaster of Paris in a brass tube B, Fig. 2, which was rigidly attached at right angles to a brass plate. This plate was screwed to the under side of the rectangular steel block A. This block had leveling screws and bolts for clamping it in position after all adjustments were made.

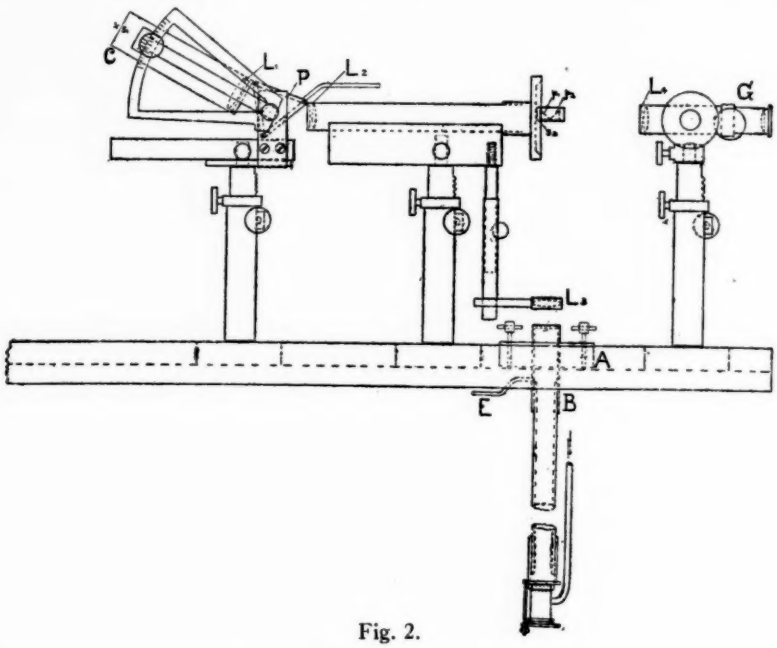

Fig. 2.

The air inclosed in the quartz tube was dry and at E was attached a tube with drying reagents so that, as the volume of the air in the quartz tube tended to decrease due to change in temperature, dry air was drawn in.

Fig. 2 is a side view showing the relation of the different parts of the apparatus. The whole was built on a heavy optical bench mounted at the side and about 20 cm. from the edge of a table. C was a collimating tube with a slit s_1 at the principal focus of the lens L_1. A flint glass prism was mounted at P in such a manner as to rotate upon an axis through its center. The lens L_2 brought the light to a focus at s_2, at which point was placed an adjustable spectroscope slit. The mounting of the prisms p_1 and p_2 not shown in the drawing, was such that a motion

of translation in the vertical plane could be had, a rotation about an axis perpendicular to the spectroscope slit, a rotation about a second horizontal axis at right angles to this one, and finally, the whole mounting was hinged at the side and by one motion of the hand could be swung around out of the field in making other adjustments, and then brought back to exactly the same position. The light was reflected down by the prism p_1, rendered parallel by the lens L_3 which was mounted with a

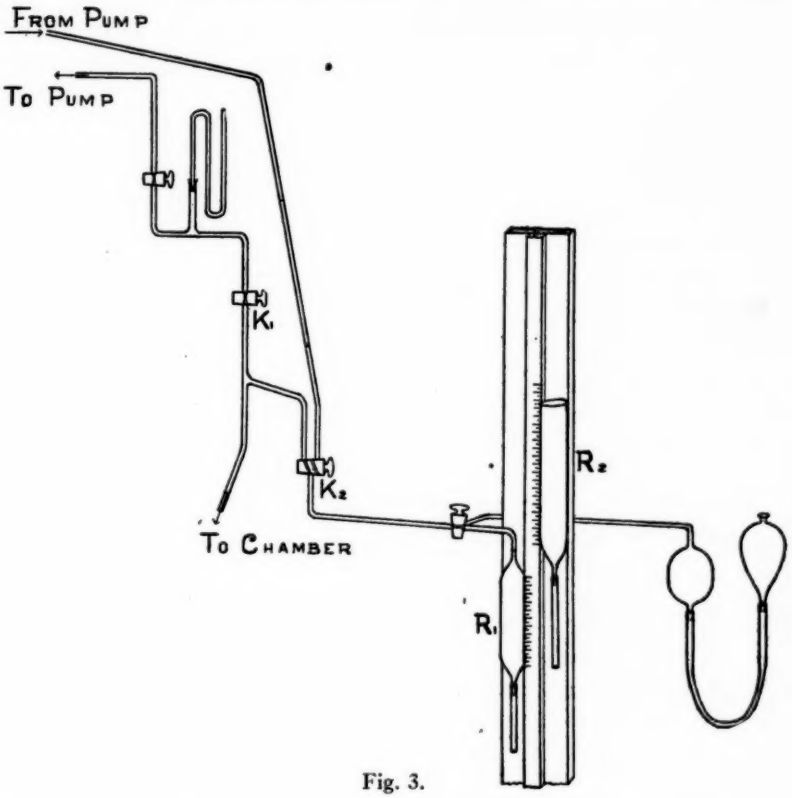

Fig. 3.

rack and pinion adjustment, was transmitted to the interference apparatus from which it was again reflected and again brought to a focus at the prisms and deflected horizontally by the prism p_2 to the observing telescope. This consisted of a short focus lens L_4 and a micrometer eye-piece fitted with cross hairs at right angles and double movable cross hairs. This telescope had a rack and pinion vertical adjustment and a lateral adjustment by means of a tangent screw.

On the lower surface of the optical cover glass was cut a small circle about 1 mm. in diameter, and the fixed cross hairs in the eyepiece were set tangent to this circle. Such a circle is easily obtained by mounting

the glass in the chuck of a small lathe and while rotating slowly, bring a diamond point against the surface of the glass, using a suitable rest.

The gas circuit is shown in Fig. 3. A mercury pump was placed at the side of the optical parts away from the table and connections made to it above the part of the apparatus just described. The parts shown in the diagram were mounted on the table near its end, being thus placed at the right of the optical parts, and the two principal stopcocks K_1 and K_2 were within easy reach while observing at G, Fig. 2. R_1 represents a cylindrical glass reservoir about 3 cm. in diameter and 30 cm. long; R_2 the mercury level reservoir was of the same diameter but somewhat longer. Both of these were mounted on the front side of a piece of studding extending to the ceiling. R_1 was mounted in a fixed position with its upper end a little above the top of the table.

R_2 was mounted on a carriage which could be moved up and down the timber by means of a cord passing over a system of pulleys at the ceiling. These cylinders were connected by pressure tubing which was wrapped with cord to prevent undue extension when cylinder R_2 was raised. Along the center of the timber were mounted meter bars for measuring the difference in height of the mercury columns. The readings upon these were made in a manner similar to that in reading an ordinary barometer. That is, brass collars of thin sheet brass were made of diameter a few millimeters greater than the diameter of the glass cylinders and these collars were mounted to move easily up and down over the cylinders. The lower ends of the collars were finished with pointers extending 1 or 2 mm. over the edges of the meter bars, also the lower edge of the collar and the lower edge of the pointer were in the same horizontal plane. The surfaces back of the cylinders were of such character as to give diffuse reflection. In reading, the collar was brought down until light could just be seen over the surface of the mercury, and the corresponding point on the meter bar read off. In this manner pressure readings could be made to an accuracy greater than 0.5 mm., but since the coefficient of expansion of the meter bars was not accurately known, nor to what extent, if at all, they were affected by the relative humidity, no attempt was made to read closer than 0.5 mm., and the final readings are given to the nearest mm.

In interference work where a large path difference is used, probably the most satisfactory light is the green light of the Cooper-Hewitt mercury lamp. This was used in the preliminary work, though it was the intention to use a series of spectral lines in the final observations on the gases studied. No source of light was found satisfactory for the work however, so the Cooper-Hewitt lamp was used throughout the

investigation, observations being made with the green and yellow lines. The mean of the wave-lengths of the yellow lines was used in the computations.

Upon a change of pressure ensuing, it is obviously impossible to count the bands for more than one spectral line. To repeat the experiment under identical conditions and count the shift of bands for a second spectral line is also impossible. This difficulty may be overcome in two or three ways. In any case the fraction of the band nearest the fixed cross hairs is determined for each system of fringes at each pressure, *i. e.*, for the fringes of each spectral line used. Then, having counted during the change in pressure the whole number of bands moved of the wave-length chosen as the standard, the exact number including the fraction is known for this wave-length. Also the fraction of a band for the other, or for each of the other of the spectral lines used is known. If the total number of bands moved is small, the integral number corresponding to the fraction or to each of them, can usually be determined at once by inspection.

If the number of bands moved is large, and the number cannot be determined by inspection, a method similar to that given by Pulfrich[1] for the determination of the change of bands in dilatometer work by the use of two or three spectral lines instead of counting the bands may be used.

Let a = the whole number of bands moved of the wave-length chosen as the standard; let δ_0 = the initial fraction, and δ_0' = the fraction after the change in pressure has taken place. Let b, δ, and δ', represent the corresponding values for a second spectral line. Then $a + \delta_0' - \delta_0 =$ the total number of bands shifted in the case of the first or standard wave-length and $b + \delta' - \delta =$ the total number of bands shifted for the second wave-length. Also

$$a + \delta_0' - \delta = N_0(1 - n_0)$$

and

$$b + \delta' - \delta = N(1 - n)$$

where N_0 and N are the total number of wave-lengths respectively in the path traversed by the light. Dividing the first equation by the second and rearranging, there is obtained

$$\frac{a + \delta_0' - \delta_0}{N_0(1 - n_0)} = \frac{b + \delta' - \delta}{N(1 - n)}$$

or

$$\frac{N}{N_0}(a + \delta_0' - \delta_0) = \frac{1 - n_0}{1 - n}(b + \delta' - \delta), \qquad (A)$$

[1] Zeits. für Inst., 1893, p. 365.

$$\frac{N}{N_0}a = \frac{1 - n_0}{1 - n}(b + \delta' - \delta) - \frac{N}{N_0}(\delta_0' - \delta_0). \qquad (B)$$

Since $N_0 = 2d/\lambda_0$ and $N = 2d/\lambda$, one has $N/N_0 = (2d/\lambda)/(2d/\lambda_0) = \lambda_0/\lambda =$ a constant, j say. Also, for the present purpose, with a given gas the ratio $(1 - n_0)/(1 - n)$ may be considered as constant $= k$ say. Then

$$ja = k(b + \delta' - \delta) - j(\delta_0' - \delta_0)$$

or

$$\frac{j}{k}a = b + \delta' - \delta - \frac{j}{k}(\delta_0' - \delta_0). \qquad (C)$$

A table can be formed the first column of which contains the successive values of a as 1, 2, 3, etc., the second column the integral parts of the product $(j/k) \cdot a$, as 0, 1, 2, 3, etc., and the third column the fractional part of the product. The quantity $\delta' - \delta - (j/k)(\delta_0' - \delta_0)$ must correspond to the fractional part. Therefore the whole number b can be obtained from the table at once.

It is obvious that this cannot be relied upon to the same degree of accuracy as the method referred to above, which is frequently used where the interference method is applied to linear measurements only. Notwithstanding this fact, equation (C) has been found very useful in the present investigation.

A more exact though more laborious method is to solve equation (B) directly for each separate case. The only unknowns in this equation are b and n and the latter can be substituted in terms of b and N, and b thus determined.

Temperature Measurements.

For those observations made at 0°, the apparatus was packed in powdered ice in a Dewar cylinder. Under these conditions, of course no question exists as to the constancy of the temperature nor of its absolute value. For the observations made at liquid air temperatures, a platinum resistance thermometer was used to determine the temperature. The wire of this thermometer was mounted by threading it through small holes punched in thin strips of mica, then other strips were laid on these and rolled into a ring about 3 cm. in diameter. Two leads were fused to each end of the thermometer wire. The ring was tied to the outside of the chamber. Since the chamber and thermometer were completely immersed in the liquid air it seems very probable that the temperature of the enclosed gas was that indicated by the thermometer.

The thermometer was calibrated by observing its resistance in steam, in ice, and in liquid oxygen. Callendar's formula was used, the δ being computed by means of the values of these resistances.

One series of observations was made on carbon dioxide at − 78°.3 C. This temperature was obtained by immersing the chamber in a mixture of CO_2 snow and alcohol.

It may be noted that for the observations at liquid air temperature the values of the indices obtained upon decreasing the pressure are slightly greater than those obtained upon increasing the pressure. This is due to the slight rise in temperature resulting from the evaporation of the liquid air during the progress of the readings. Except in one or two cases especially noted, this change was slight. The temperatures given at the head of the tables are the mean temperatures where the variation amounts to as much as one and one half or two tenths of a degree.

During the preliminary work on the apparatus a number of readings were made on atmospheric air, mainly at pressures of about one atmosphere. The carbon dioxide and water vapor were removed from the air. Some of the observations were made at room temperature and some at 0° C. Reducing the former to 0° and all to 76 cm. pressure by means of the relation $(n_{t,\,p} - 1)/\rho_{t,\,p} = (n_{0,\,76} - 1)/\rho_{0,\,76}$, there is obtained by taking the mean of a number of these the value 1.000 2922 for the index of refraction of the green mercury line, and 1.000 2914 for the yellow line, with a probable error of 0.000 0003. In some of these readings the pressure was obtained from roughly balanced mercury columns and may have been incorrect to 1 or 2 mm. If a corresponding series had been made when the apparatus was in its final working condition, the probable error would certainly be very much less.

The value of the index of the D-line obtained by means of a dispersion formula from the above stated values is in very good agreement with the values tabulated by Scheel.

Two or three sets of observations were also made on air at liquid air temperatures, one of which is given in the table below. The Dewar cylinder used to contain the liquid air was a poor one and the liquid air evaporated rapidly, thus causing a considerable rise in temperature during the course of the readings. The first temperature was read near the beginning and the second temperature at the conclusion of the observations.

Atmospheric Air. −189°.0, . . . − 188°.0 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
73.5	52.42	9,610	49.37	9,577
00.0	——	——	——	——
50.7	35.69	6,543	33.68	6,533
73.5	51.91	9,516	48.92	9,490
91.4	64.91	11,899	61.16	11,864
73.5	51.78	9,496	48.78	9,466

The values of the indices of air at liquid air temperature are also in good agreement with those obtained by Scheel, the only values available for comparison.

PREPARATION OF THE GASES AND OBSERVATIONS.

Hydrogen.

Aside from the numerous preliminary observations on air, the first gas studied was hydrogen. It was obtained from a cylinder of electrolytically prepared gas, and an attempt was made to remove the traces of

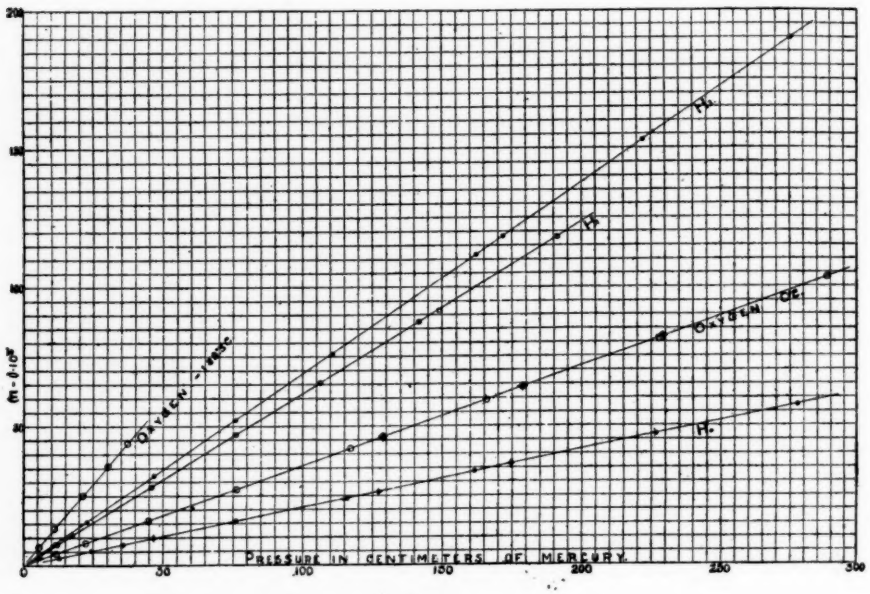

Fig. 4.

oxygen, carbon dioxide, and water vapor. A series of observations was made at liquid air temperature, the pressure being carried only to 192 cm. of mercury. This gas was then replaced by another quantity, which was more carefully prepared. After making a large number of observations on it, in order to know definitely regarding its purity, analyses were undertaken. These were made by means of the explosion pipette. The hydrogen proved to be very impure. Whether the contamination occurred at the time of the preparation of the gas, or from a leak in the pump during several days elapsing before the analyses were made, could not be determined, but probably resulted largely from the latter cause. Some trouble at one stopcock in the pump was remedied and another quantity of gas prepared, greater care being used in its preparation.

With this, one series of observations was made at − 191°.1 and one at 0°. These observations are given in the table, and the corresponding curves shown in Fig. 4. Analyses again made at the end of the work on one sample of gas drawn from the pump at the time of preparing the gas and on samples drawn at the conclusion of the observations gave the same results, and showed that this gas was also impure. The results were: hydrogen 88 per cent., oxygen 2 per cent., and though no test was made for it, the remainder in all probability was nitrogen. While it is granted that the observations on this gas are of no great value, yet since the composition of the gas is known, they may be of some interest.

Oxygen.

The oxygen also was obtained from a cylinder of the electrolytically prepared gas. Analyses of the gas drawn directly from the cylinder showed about two per cent. impurity. A test for hydrogen showed about one per cent. present. The remaining impurity was probably largely nitrogen, due to the absorbed air in the water from which the gas was made.

Because of the difficulties involved, no attempt was made to remove the trace of nitrogen, but the gas was passed over red-hot copper to remove the hydrogen, over solid caustic potash and through drying tubes including a tube immersed in liquid air. A pump was attached and the whole system of tubes containing reagents exhausted several times after allowing oxygen to enter, in an attempt to remove all traces of gases formerly contained in the tubes. The pump and gas system was also washed out with the gas previous to filling. Before the observations were begun, samples of the gas were drawn from the pump and an analysis made. Analyses were again made at the completion of the work. These were in good agreement and showed between one and two per cent. of impurity.

Two series of observations were made, one at 0° and one at − 189°.3. The observations are given in the table and the corresponding curves shown in Fig. 4. The readings at the latter temperature were continued until liquefaction began.

Nitrogen.

The nitrogen was prepared from atmospheric air by the removal of the oxygen and the carbon dioxide. Air was passed through a series of tubes containing pyrogallol, calcium chloride, lumps of phosphorus, and through phosphorus pentoxide and through a tube immersed in liquid air. Tests were made for oxygen, and it was found that a relatively large per cent. of oxygen still remained in the gas after it had passed slowly through this system. Another reservoir was then arranged so that the gas could

be passed back and forth over the phosphorus and the two drying tubes. This was continued until analysis showed only a small fraction of one per cent. of oxygen. At the completion of the observations on the nitrogen, further analyses showed about the same percentage.

Three series of observations were made on nitrogen; one at 0°, and two at liquid air temperatures. At 0° the gas is well above its critical temper-

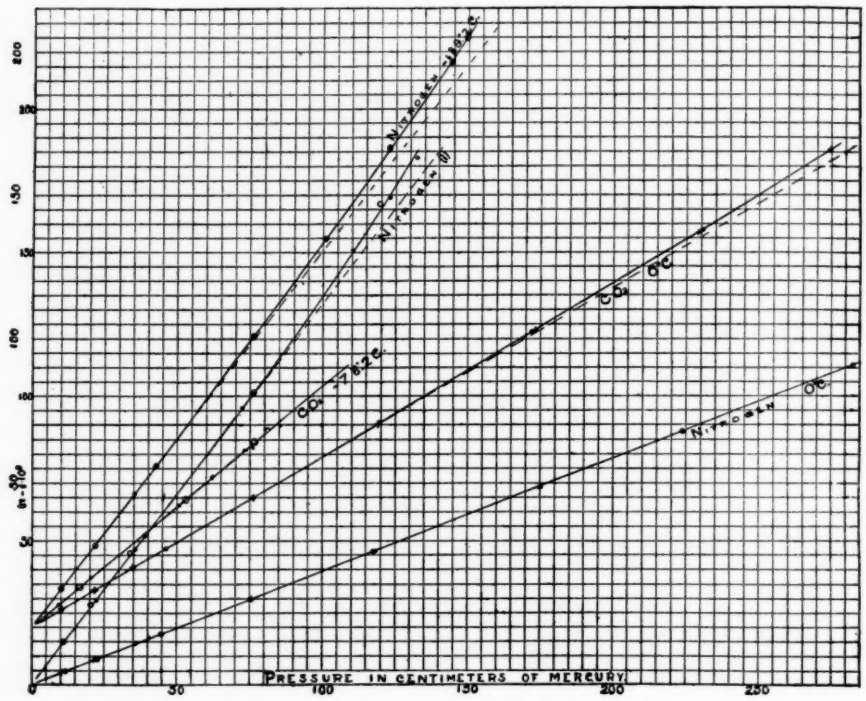

Fig. 5.

ature, Boyle's Law is applicable, and the relation between $n - 1$ and the pressure is a linear one, or what amounts to the same thing, the relation between $n - 1$ and the density times a constant. In the case of the observations at liquid air temperatures, considerable deviation from linearity is found commencing at about one atmosphere. (See Fig. 5.) Curve (1) shows a little irregularity in the observations. The series was repeated with liquid air which had been allowed to stand for twenty-four hours, thus enabling one to work at a slightly higher temperature. These readings are shown in curve N (2). It may be noted that the observations were extended to a higher pressure before liquefaction occurred. The general form of curve is the same.

Carbon Dioxide.

Travers[1] would lead one to think that very pure gas can be obtained from the commercial product sold in steel cylinders. Acting upon this assumption, gas from a cylinder was passed through drying tubes and frozen in a tube with closed end immersed in liquid air. This tube was also connected with the pump and gas circuit, and upon closing the connection to the tube and opening that from the tube to the pump it could be exhausted to the vapor pressure of the carbon dioxide at liquid air temperature, thus removing air, etc., contained in the gas. Upon removing the tube from the liquid air and allowing its temperature to rise, the carbon dioxide would pass over into the pump and gas circuit. Analysis of the gas prepared in this manner showed about 75 per cent. carbon dioxide. An analysis of the gas direct from the cylinder showed about 95 per cent. carbon dioxide. The only explanation of this appears to be that the gas probably came from Saratoga Springs and contained one or more of the marsh gas series having a higher vapor pressure than the carbon dioxide. Consequently when the frozen mixture was removed from the liquid air, a mixture was obtained containing less carbon dioxide than the gas from the cylinder.

A Kipp generator was next set up and carbon dioxide was generated from acid on marble and purified in the same manner as that just described, except that there was added to the system of drying tubes a tube immersed in carbon dioxide snow and alcohol to remove further traces of moisture. The pump and gas system was washed with the gas as in the preceding cases. Analyses of samples of the gas thus prepared taken from the pump before the observations were begun, all showed about one half of one per cent. of impurity. In this respect the results were more satisfactory than in the case of any of the other gases.

Two series were made at 0° and one at − 78°.2. In the case of the former temperature, the circles on the curve represent the readings for one series and the crosses those for the other. It may thus be seen how closely the observations agree. Furthermore the second series was made on a different mass of gas.

For the higher pressures at 0° there is a very appreciable deviation from linearity.

In the case of the curve at − 78°.2 the readings were continued until condensation occurred, then the pressure was decreased somewhat and new readings taken, then the pressure again increased and so on. In this

[1] Study of Gases, p. 49.

way a number of observations in that region was obtained. These are indicated in various ways in the diagram. The variation of the values is rather large, due in part to the error of observation, as some of the readings were obtained with difficulty, two thirds or more of the field being obscured by the carbon dioxide snow upon the surfaces of the glass plates. Also the pressures could not be read with great exactness under such conditions because of the changes in volume taking place.

Hydrogen (1). −187°.5 C.

Pressure.	Green.	
	Bands.	$(n-1)\cdot 10^7$.
5.6	1.91	350
12.0	4.09	750
17.4	5.99	1,098
45.8	15.37	2,818
106.7	35.69	6,543
141.1	47.59	8,724
191.8	64.38	11,802
149.4	49.89	9,146
76.1	25.19	4,618

Hydrogen (2). −191°.1 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
11.3	4.30	788	4.02	779
22.7	8.49	1,556	8.00	1,552
46.7	17.56	3,219	16.40	3,181
76.0	28.37	5,201	26.59	5,158
110.7	41.38	7,585	38.88	7,542
162.3	60.86	11,157	57.01	11,059
171.9	64.37	11,807	60.38	11,713
222.0	83.38	15,292	78.53	15,182
275.5	103.48	18,986	97.47	18,908
221.9	83.14	15,248	78.30	15,189
171.5	64.14	11,765	60.43	11,723
122.3	45.64	8,365	42.95	8,331
75.5	28.08	5,155	26.47	5,135
36.2	13.51	2,484	12.68	2,460
5.5	2.14	392	2.02	391
11.8	4.49	823	4.19	813
23.2	8.72	1,599	8.18	1,587
31.7	11.85	2,172	11.10	2,153
76.1	28.32	5,195	26.51	5,143

Hydrogen (2). 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
12.8	1.45	266	1.29	250
24.4	2.81	515	2.62	508
35.6	4.04	741	3.76	729
76.15	8.62	1,580	8.10	1,571
116.0	13.08	2,398	12.30	2,386
162.6	18.29	3,353	17.26	3,348
226.5	25.52	4,678	24.06	4,666
277.7	31.25	5,729	29.41	5,705
226.2	25.47	4,669	24.02	4,660
174.3	19.66	3,604	18.51	3,591
127.3	14.28	2,618	13.48	2,615
76.0	8 57	1,571	8.06	1,563
46.6	5.22	957	4.96	962
25.5	2.90	532	2.76	535
0.0	——	——	——	——
28.4	3.23	592	2.99	580
76.1	8.60	1,576	8.11	1,573

Oxygen 0° C.

Pressure.	Bands (Gr.).	$(n-1)\cdot 10^7$.	Bands (Yl.).	$(n-1)\cdot 10^7$.
11.6	2.32	426	2.19	427
22.2	4.31	790	4.09	793
44.9	8.72	1,599	8.17	1,585
76.2	14.83	2,718	13.98	2,712
117.3	22.84	4,187	21.42	4,155
165.9	32.29	5,919	30.38	5,893
227.6	44.29	8,119	41.68	8,085
288.7	56.35	10,329	52.00	10,289
229.1	44.76	8,205	42.16	8,178
178.7	34.67	6,356	32.71	6,345
128.9	25.14	4,609	23.69	4,595
76.3	14.92	2,735	14.05	2,725
44.8	8.79	1,611	8.29	1,608
13.9	4.76	873	4.45	863
0.0				
76.7	14.98	2,746	14.15	2,745

Temperature, − 189°.9 C.

5.4	3.62	664		
11.0	7.24	1,327		
21.2	13.69	2,510		
30.2	19.45	3,565		
37.2	23.89	4,380		

Nitrogen. 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10$.
11.7	2.55	468	2.36	458
22.6	4.87	893	4.58	888
44.8	9.58	1,756	9.00	1,746
75.7	16.20	2,970	15.27	2,962
117.5	25.13	4,607	23.63	4,584
175.4	37.49	6,873	35.32	6,851
224.0	47.95	8,790	45.16	8,760
282.8	60.46	11,083	56.95	11,047
223.9	47.90	8,781	45.14	8,754
174.8	37.40	6,858	35.24	6,836
118.4	25.34	4,645	23.82	4,621
75.6	16.21	2,970	15.23	2,954
36.0	7.74	1,419	7.29	1,414
0.0	——	——	——	——
10.4	2.29	420	2.15	417
21.4	4.64	851	3.98	838
40.7	8.75	1,604	7.88	1,594
75.6	16.17	2,964	14.89	2,954

Nitrogen. — 191°.6 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
11.0	8.17	1,498	7.59	1,472
20.2	15.19	2,785	14.22	2,758
33.9	24.91	4,566	23.36	4,532
75.8	56.42	10,343	52.09	10,105
119.6	91.07	16,695	84.70	16,430
		— 190°.6 C.		
72.6	53.21	9,754	50.20	9,738
35.6	25.67	4,706	24.18	4,691
0.0				
10.8	7.86	1,441	7.37	1,430
22.2	16.06	2,944	15.16	2,941
39.0	28.11	5,153	26.44	5,129
76.3	55.82	10,233	52.61	10,205
110.4	82.28	15,083	77.59	15,052
123.0	92.28	16,924	87.03	16,883
132.3	99.77	18,299		

Two hours elapsed between the first and second sets of the above readings.

In the curve, $N(1)$, Fig. 5, the point for the pressure of 75.8 cm. pressure in the first set should be four tenths of a division higher, and the point for the pressure of 72.6 cm. of pressure in the second set should be between three tenths and four tenths higher.

Nitrogen. — 189°.2 C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$
10.1	7.27	1,333	6.81	1,321
21.9	15.72	2,882	14.82	2,875
42.8	30.49	5,589	28.71	5,569
76.4	55.09	10,099	51.87	10,062
101.0	73.60	13,493	69.35	13,453
122.8	90.69	16,625	85.45	16,576
143.5	107.08	19,629	100.87	19,567
149.5	111.81	20,497	105.45	20,458
143.4	106.98	19,611	100.83	19,560
122.8	90.50	16,590	85.32	16,551
100.9	73.48	13,470	69.29	13,441
76.2	54.77	10,040	51.64	10,018
35.5	25.19	4,618	23.74	4,605
0.0				
76.7	55.02	10,086	51.86	10,060

Carbon Dioxide. 0° C.

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
10.4	3.44	631	3.26	632
21.7	7.04	1,291	6.66	1,262
46.3	14.91	2,733	14.02	2,720
76.3	24.54	4,498	23.12	4,485
119.5	38.59	7,074	36.39	7,061
171.9	55.90	10,248	52.67	10,217
230.3	75.28	13,800	70.89	13,752

Series No. 2.

10.9	3.50	642	3.33	646
21.6	6.97	1,278	6.54	1,269
34.9	11.19	2,084	10.46	2,029
76.3	24.45	4,482	23.00	4,462
119.1	38.39	7,038	36.15	7,013
173.1	56.23	10,308	52.91	10 264
229.6	74.91	13,732	70.48	13,672
274.9	90.05	16,508	84.81	16,452
228.8	74.64	13,683	70.32	13,641
173.1	56.20	10,302	52.91	10,261
118.6	38.31	7,023	36.03	6,989
75.8	24.34	4,462	22.86	4,435

Carbon Dioxide. $-78°.3$ *C.*

Pressure.	Green.		Yellow.	
	Bands.	$(n-1)\cdot 10^7$.	Bands.	$(n-1)\cdot 10^7$.
16.6	7.53	1,380	7.10	1,377
53.0	24.10	4,418	22.74	4,411
76.6	35.10	6,434	33.06	6,413
0.0	——	——	——	——
9.3	4.23	775	3.98	772
20.6	9.33	1,710	8.78	1,703
51.0	23.04	4,224	21.72	4,213
76.1	34.53	6,330	32.49	6,303
85.4	38.13	6,990	35.97	6,978
73.4	33.33	6,110	31.40	6,091
81.1	37.25	6,829	35.07	6,803
73.0	33.27	6,099	31.39	6,089
62.4	28.48	5,221	26.80	5,199
50.7	23.09	4,233	21.75	4,219
0.0	——	——	——	——
76.1	34.01	6,235	32.02	6,211

From the various curves we have seen that within the limits of accuracy of observations of the experiments, the relation between the indices of refraction and the pressure is a linear one, except for the case of carbon dioxide at 0° and for nitrogen at liquid air temperature. In other words, the relation between the refractive indices and the density as computed by Boyle's law is a linear one.

For the carbon dioxide at 0° and the nitrogen at liquid air temperature the densities have been computed by means of van der Waal's equation. The values of the constants a and b of the equation were obtained from the critical pressure and temperature of the respective gases. For carbon dioxide the values of the critical pressure given in the tables vary rather widely. A value of 5,700 cm. of mercury was chosen, and 304° abs. as the temperature. By the use of these values were obtained, $a = 137{,}000$ and $b = 0.942$. The curve showing the relation between the resulting densities and refractive indices is given in Fig. 6. The points fall very accurately on a straight line.

The critical values of nitrogen as used were, 2,660 cm. and 146° abs. The resulting values of the constants are $a = 126{,}070$ and $b = 1.325$. The densities were computed for the pressures in the series $N(2)$. In this series the values of the pressures for increasing values and those for decreasing values are very near each other, in some cases identical. Where they are not identical the mean of the two was taken, also the corresponding mean of the indices of refraction in plotting the curve.

The curve is shown in Fig. 6. The points lie on a straight line except the last two.

In order to compare further the variation of the refractive indices with the densities as obtained by the two methods, and also to compare the formula of Gladstone and Dale with the Lorentz-Lorenz formula, the table on page 182 is given. The first column contains the pressure and

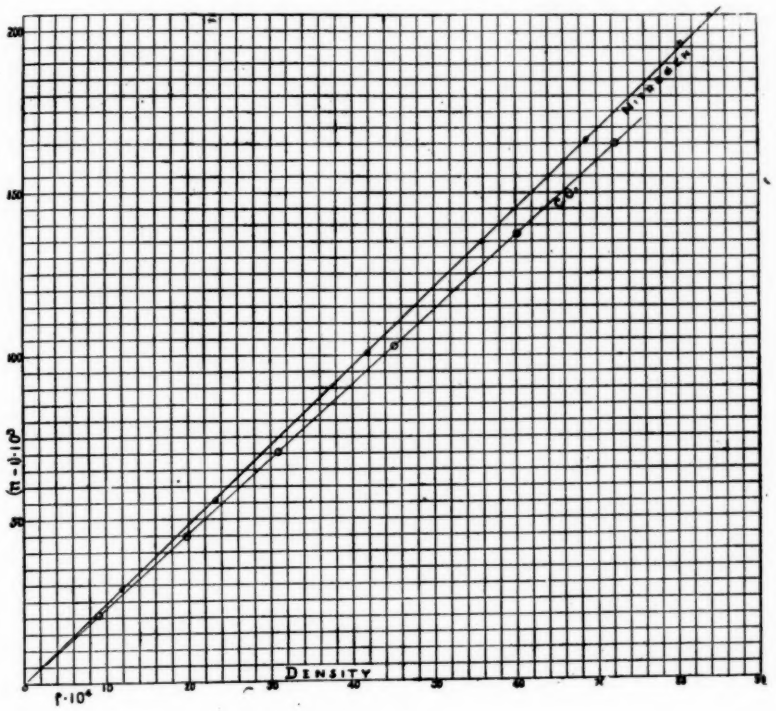

Fig. 6.

the fourth the corresponding refractive indices; the second column contains the densities as obtained by Boyle's law, the third the densities as obtained by using van der Waal's equation, the fifth the values of the constant as given by Gladstone and Dale's expression, using the values of the densities in the second column, the sixth the values of the constant as given in the third column, and the seventh and eighth columns the corresponding values of the constant of the Lorentz-Lorenz formula.

It may be noted that the variation of the values in the last column is two per cent. and the variation of those in the sixth column also two per cent.

It may be of interest to state that for nitrogen at 0° C. (excluding the

two lowest pressures), computing the densities by Boyle's law and using the Gladstone and Dale expression, the values of the constant vary only about two tenths of one per cent.

Nitrogen. $-189.2°$ *C.*

Pressure in Cm. Mercury.	Densities Obtained by Using Boyle's Law.	Densities Obtained by Using van der Waal's Equation.	Indices of Refraction.	Values of the Constant in Gladstone and Dale's Expression Using Densities from Column Two.	Values of Constant in Gladstone and Dale's Expression Using Densities from Column Three.	Values of the Constant in the Lorentz-Lorenz Expression Using Values of the Densities from Column Two.	Values of the Constant in the Lorentz-Lorenz Expression Using Values of the Densities from Column Three.
10.1	0.000543	0.000544	1.0001333	0.2455	0.2450	0.1637	0.1633
21.9	.001177	.001187	.0002882	.2448	.2434	.1632	.1623
42.8	.002301	.002328	.0005589	.2429	.2401	.1619	.1600
76.4	.004101	.004194	.0010099	.2462	.2408	.1641	.1605
101.0	.005424	.005589	.0013493	.2481	.2414	.1658	.1609
122.8	.006601	.006874	.0016625	.2518	.2419	.1678	.1612
143.5	.007709	.008054	.0019629	.2546	.2438	.1697	.1624
149.5	.008036	.008411	.0020497	.2551	.2437	.1699	.1623

In conclusion the writer wishes to express his thanks to Professor E. L. Nichols for many kindnesses and to Professor J. S. Shearer, under whose direction the work was undertaken, for many helpful suggestions.

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THE THERMAL COEFFICIENT OF CONTACT ELECTROMOTIVE FORCE.

By Harry C. Burbridge.

IN looking back over the development of electrical knowledge we find many experimenters who have made a study of contact electromotive force. Their work has been extensive in its range and carefully done and the discussion of it has contained the defense of many widely differing theories. Yet, with all the investigation that has been given to this subject, the effect of temperature upon the potential difference of contact has received but scant attention. A few investigators have attempted to determine it but their efforts, with one exception, have proven almost fruitless. It would seem unquestionable that this temperature effect would have an important bearing upon the explanation of the original phenomenon and that its determination is worthy of extended effort.

Peculiarly enough, from the first attempt ever made to measure this temperature effect came some of the most satisfactory results. This attempt was made by Cavallo,[1] an experimenter in England, at some time previous to the year 1795. He used the very simple means of dropping a piece of metal from his hand upon an insulated tin plate, shaking it off, and then by applying the plate to a multiplier, increased the charge sufficiently to be tested with an electroscope. This process would, of course, give the contact potential difference between tin and the metal used. He found in this way, zinc positive to tin and silver; bismuth negative to tin, but lead and platinum positive to it. On heating the different metals, he found zinc, tin, silver and bismuth to become more positive, while lead and platinum became more negative. It appears then that he placed most of the metals in their proper order both as to their potential and the change of it by increased temperature, though the magnitude of this change could not be measured with his apparatus. This, of necessity, terminated his work and it was not until 1879 that further attempts were made to perform this experiment. At that time Knott[2] made measurements on the potential difference between two plates of the same metal, one being heated. He found iron, copper,

[1] Nicholson's Journal, Vol. I., page 184, 1802.

[2] Knott, Proc. Royal Soc. of Edin., No. 105, p. 362, 1879.

zinc, and tin to become negative when heated, and the effect to increase with the temperature. This change, however, was permanent, as it persisted after the metals were cooled, hence what he determined was the relation of a hot and oxidized surface to a normal one of the same metal. This then was not a true temperature effect and as his work ceased here it is of no practical value. Again in 1882, Von Zahn tried the same experiment, hoping to find it related to the Seebeck effect. His conclusions are not available.

It is evident therefore that the data given by Cavallo nearly a century before are as valuable as these later data so that it is in the results of Erskine-Murray's[1] work alone that anything dependable is to be had regarding the temperature effect. The range of his experiments was not large either in the number of metals used or in the temperature differences. No temperatures were carried beyond 70° and some to only 30°. Also the determination of the temperature was very rough, being estimated by touching with the fingers in all plates except one.

When these conditions are considered in regard to the data given by Erskine-Murray, and it is remembered that these are the only data of any consequence that have been published, it would seem that the present endeavor to measure the temperature effect would be far from mere repetition. It was undertaken with the purpose of adding to the other data upon contact electrification, some reliable values of its temperature coefficient.

The method of the following experiments was essentially the same as that used by Erskine-Murray, namely, a null method. It differs from it, however, in one respect and in that same respect from all other experiments on the potential difference of contact. Instead of using parallel plates two telescoping cylinders were used, the inner being much shorter than the outer so that it could be put well inside it. No matter what theory of contact potential difference one holds to, it is agreed that between the two surfaces there is an electrical field. This form for the two metals was chosen therefore that the metal composing the inner cylinder might be wholly in the field of the other, and not partially so as in the case of plates.

A sensitive electroscope was tried at first but discarded in favor of a Dolazalek electrometer. The sensitiveness of this instrument more than compensated for its larger capacity, and its reliability left no question as to the advantage of its use. The heating of the inner cylinder was first done by raising it into a steam jacket but it proved more satisfactory to fill the cylinder with water and use an electric heater, and this method was followed throughout.

[1] Erskine-Murray, Phil. Mag., Vol. 45, p. 398, 1898, "On The Volta Electricity of Metals."

The apparatus was arranged as shown in Fig. 1. The outer cylinder (*A*) was made of commercial sheet copper about 1.2 millimeters thick and formed into two half cylinders 94 mm. in diameter and 240 mm. in length. The halves were held together by two adjustable copper bands. The base (*B*) was turned from plate copper 8 millimeters thick and the

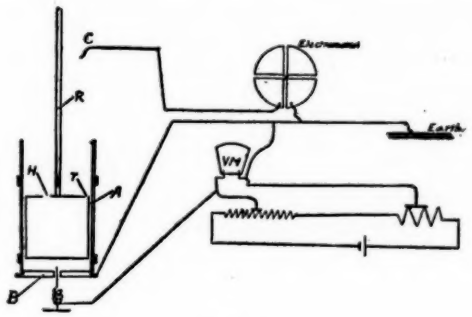

Fig. 1.

outer part thinned to 5 mm., leaving a circular table 3 mm. high in the center, over which the cylinder (*A*) fitted. This base (*B*) rested on a triangular wooden table with three screw-feet for leveling. In the center of the base was a three-millimeter hole fitted with a hard-rubber insulator. Through this passed a No. 22 brass wire, the portion below the base being coiled into a spring to make the contact adaptable.

This construction of cylinder and base allowed for easy cleaning. On removing the cylinder (*A*), the base was unobstructed and the cylinder itself being in two parts, both inside and outside surfaces were readily accessible.

The different metals investigated were made into the form of hollow cylinders as (*I*), closed at both ends. They were each 86 mm. in length and diameter, thus leaving about 8 mm. between the walls of (*A*) and (*I*). These inner cylinders were cast from the metals used, with one end left open and a plate cast for this. Both parts were turned down to about 5 mm. thickness, the top plate carefully fitted in and then spun firmly in place. When necessary the inside edge of the top plate was coated with solder to insure a strong joint, but in such cases care was taken that no solder was exposed on the outer surface of the finished cylinder. In some cases where casting was not convenient or where a very pure, metallic surface was desired, cast cylinders were electroplated with the metal to be tested.

When in use, the cylinder (*I*) was carried on the vertical rod (*R*) which slid in guides. A cord fastened to the side of (*R*) raised and lowered this

cylinder by passing over a pulley above the top guide and thence to a counter-weight hung over a second pulley at the edge of a table. On this table were placed the telescope and scale for use with the electrometer and also the voltmeter and potential divider. With this arrangement the cylinder (*I*) could be raised and lowered and the movement of the electrometer needle observed at the same time. Adjustable stop-blocks with rubber pads were placed on the rod (*R*) and were set to allow the cylinder (*I*) to be lowered as close to the base (*B*) as desired and raised to just touch the flexible wire contact (*C*) leading to the electrometer.

Each inner cylinder (*I*) had a rod of the same metal 13 mm. long screwed into the center of the top. Into this was screwed a wooden piece of about the same length and the wood in turn joined to the rod (*R*) by a connection of hard rubber. The rubber served to insulate the cylinder electrically, while the wood was found necessary to keep the rubber from being softened too much by the heat from the cylinder.

In the top of the inner cylinder (*I*) and near the center a hole (*H*) was bored large enough to admit a heater made from a quarter-inch fiber rod wrapped with No. 22 resistance wire. On the opposite side of the center and flush with the inner surface a smaller hole (*T*) was bored through which a stirrer or thermometer could be inserted. The stirrer was made of stiff wire with a strip of sheet metal soldered on one end at right angles and short enough not to strike the heater. By rolling the handle of the stirrer between the thumb and finger, the blade could be moved rapidly through the water in the cylinder at any depth. This rapid stirring allowed the cylinder to be heated very uniformly. When the desired temperature was reached the stirrer was replaced by a thermometer. The opening (*T*) was located with the purpose of bringing the thermometer as close to the outside surface as possible so that the temperature it registered would be closely that of the surface.

The potential divider was of 90 ohms resistance with a ten-ohm auxiliary of coarser wire to allow more delicate adjustment. One storage cell and these rheostats were connected in series and the potential difference between the sliding contacts on the rheostats was indicated by a voltmeter reading direct to .02 volt. Thus by estimating the tenths of a division the potential difference could be determined to .002 of a volt.

The needle of the electrometer was charged to 250 volts and with the scale distance used gave a deflection of 50 cm. to the volt. The ratio of its capacity to the capacity change on separating the cylinders (*A*) and (*I*) was such that the throw equalled what the permanent deflection would have been for the same difference of potential. Thus .01 of a volt between the quadrants gave a deflection of 5 mm. and this same

difference between the inner and outer cylinders (*A*) and (*I*) gave a throw of 5 mm. From this it is evident that a throw of 1 mm. corresponds to .002 of a volt between the cylinders, which was the smallest quantity that could be read on the voltmeter. Though contact difference of potential is usually given to .001 of a volt there was nothing found to justify this. When it is considered that a clean surface at room temperature will often vary .003 or .004 of a volt in a few minutes, and when heated, as much as .006 or .008 inside of a minute, it will be seen how useless any effort toward accuracy to thousandths would have been.

The outer cylinder was carefully prepared by thoroughly cleaning with emery cloth, both the inner and outer surface of the walls and base, until every portion was bright. The surfaces were finished with the finest emery cloth and kept clean by handling only with soft, dry cloths. This left a surface almost polished in appearance, but covered with light scratches from the very fine particles of emery. It was expected that these surfaces would have to be repolished frequently, but this was not found necessary. By allowing nothing moist to come in contact with them no change could be noticed after the elapse of two or three months. The close agreement of the readings taken on the potential difference between the cylinder and a given metal, even when these readings were some weeks apart, indicated also that there was no change electrically. For surfacing the inner cylinders the finest emery cloth was likewise used. Their appearance was as described above for the outer cylinder. This surface was taken as standard, and all measurements were upon metal surfaces so prepared.

With this outer cylinder as the metal of reference, the procedure for taking a set of readings was as follows: a cylinder of the metal to be tested was put in a lathe and turned with the emery cloth held against it. The cloth was moved very little lengthwise so that the scratches were all nearly parallel to the base. On the ends the cloth was kept stationary so that all the scratches were concentric circles. The particles of metal clinging to the cloth were removed every few seconds by snapping with the finger and a fresh piece taken frequently to insure as clean a surface as possible. This process was continued until every part was bright, then a soft cloth was rubbed over the cylinder to remove all metallic dust and particles of emery. The cylinder was then reversed to complete the polishing, the finished end being wrapped in cloth to protect it from the jaws of the lathe.

The cylinder was then screwed firmly onto the sliding rod (*R*) and usually its potential with reference to the outer cylinder was determined at that time. It was then lowered into the outer cylinder and allowed

to stand over night. As has been frequently noted before, the value immediately after polishing was not permanent, consequently sufficient time was allowed before taking a set of measurements to permit the potential difference to become more nearly fixed. On beginning a set of measurements the following day, readings were taken ten or fifteen minutes apart for a half hour or longer until the potential difference seemed quite constant. This was done because it was found that the first reading always indicated the inner cylinder more positive to the outer than was permanent. The potential difference would usually fall very rapidly at first, then more slowly to a quite permanent value in about twenty minutes. The reason for this is not apparent.

When this value was reached the temperature of the inner cylinder was taken by inserting a thermometer. The temperature of the outer cylinder was obtained by using a thermometer with its bulb resting against the base (*B*). Most of the bulb was exposed to the air but the cylinder was also, so that this seemed as good a means as was necessary to determine the average temperature throughout the cylinder. It proved sufficiently accurate to show that the radiation from the hot cylinder, though it was inside the outer one only long enough to make contact and be lifted out, continually warmed it. This increase in temperature amounted to as much as five or six degrees when the readings on the inner cylinder were taken as high as 90°.

With these records made, the heater was placed in the inner cylinder and the thermometer replaced by the stirrer. The current was allowed to flow through the heater for the time found necessary by trial to raise the temperature of the cylinder and its contained water about ten degrees. The stirrer was used continually that the whole surface of the cylinder might be heated uniformly. The heater was then removed, and the water well stirred and the stirrer removed. The potential divider was at once adjusted until on lifting out the inner cylinder and touching it to the contact point (*C*), the electrometer was unaffected. The potential difference was read from the voltmeter and a thermometer placed in the cylinder. The voltmeter reading and that of the thermometer against the outside cylinder were recorded, and that of the inner cylinder as soon as it reached its highest point. This gave the temperature of the inner cylinder immediately after the potential difference was measured so that the cooling during the time required to adjust the potential divider did not necessitate a correction. The cooling itself was never rapid enough to prevent the easy adjustment of the potential divider as, at the highest temperature, the rate was only one degree in four minutes which was usually longer than necessary to set the divider. This process

was repeated until the maximum temperature was reached. The cylinder was then brought back to room temperature in intervals of approximately 10° by taking out some of the hot water and replacing it with cold. All readings were taken after each interval in the same manner as during the heating.

All the original data were corrected as found necessary when the instruments used were tested. The fixed points of both thermometers were determined and corrections made accordingly. In addition the readings of the one used in the inner cylinder were corrected for the length of the mercury thread exposed. This was done by putting the same length of the stem as went into the cylinder, into a steam bath and noting the difference between the reading then, and that when the whole length was immersed. The readings of the cylinder temperatures were then corrected by the fractions of this difference corresponding to the length of the exposed mercury thread. With these corrections probably no temperatures are in error by more than one or two tenths of a degree. Because of the corrections to the voltmeter readings they neither end in all odd nor all even numbers, but as stated before they are accurate to only 2 units in the last place.

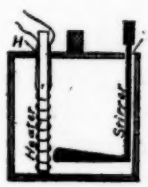

Fig. 2.

As would be expected, the temperature of the outer cylinder did not remain constant while a set of readings were being taken. This meant that the cylinder's potential changed somewhat from one measurement to the next and consequently, the potential difference observed was in error by the amount of this change. The correction to be applied would have been easily found had the coefficient of copper been known, but not being so, a proper method of determining it seemed difficult to find. It is not to be overlooked that placing the inner cylinder, at perhaps 80 or 90 degrees temperature, within a few millimeters of the outer copper base even for only a second or two necessary for each contact might easily heat the very surface of this base far above the temperature of the remainder. If then it is the surface that determines the potential difference, this effect might cause the readings to be considerably below the true value because the real temperature difference would be far less than the one measured. However, as there seemed no way to prevent this if it should exist and no way to measure it so that a correction could be applied, it is disregarded in the following.

After some consideration the following method of correcting for the temperature change of the outer cylinder appeared the most reasonable one to be applied. It was assumed that its temperature coefficient was

the same as that of the inner cylinder made of copper. Then the four most consistent sets of data on the temperatures and the potential differences of the two copper cylinders were tabulated for increasing temperature only. Each number was subtracted from the one below it in its own column, thus giving a table of the change in voltage from each temperature reading on the inner cylinder to the following one, and also whatever increase in temperature the outer cylinder had taken on. Each of these potential changes were then corrected by proportion. Thus, if from the previous reading the potential had risen .008 volt, the temperature had increased 10.8°, and the outer cylinder at the same time had become 0.6° warmer, then the increase in voltage was not due to 10.8° because the voltage is measured from a base that has risen 0.6°. The measured rise in potential was then due to 10.8 less 0.6 degree, or 10.2°. Hence, if the base had not risen in temperature the voltage change would have been (.008 × 10°.8)/10°.2 volts. This method of correction was applied to each change of potential and then by adding these differences the readings were obtained that would have resulted, had the outer cylinder remained constant in temperature. These values were plotted and the straight line drawn that best fitted each set of readings up to about 50° temperature. The slope of the line for each set was determined and the average of these slopes taken. This average value was then considered the temperature coefficient of the outer copper cylinder. All the readings of the potential difference were corrected by the use of this coefficient for the number of degrees which the outer cylinder differed from 20°. Thus all potentials given are with reference to this copper cylinder at 20° temperature.

In getting at the correction for the change in temperature of the outer cylinder it was assumed that the relation between the voltage and temperature was a straight line for the range used, of about 30°, and the data justified this assumption. However it would not seem allowable to assume a straight line relation for the whole range. When it is considered that a satisfactory explanation of the Volta effect has not yet been set forth, it would not seem worth while to hazard a guess as to the action that underlies the effect of temperature. Hence no form of curve can be assumed, and the variations from it considered merely errors of measurement.

Besides this, another difficulty arises in the interpretation of the results obtained, because the values are not uniform and consistent but widely varying. Despite the utmost care in preparation to have the surface always the same yet the potential difference at room temperature for the same metal against the copper outer cylinder would be quite different

from one day's surfacing to another. This was not so serious a difficulty, as it was the change and not the absolute potential difference which was sought. The serious thing was the widely differing values of the temperature coefficient obtained which made a reliable determination of it most difficult. The temperature-voltage curve for a given metal, with falling temperature, neither came back accurately on the rising temperature curve, nor differed from it in any consistent way. Taken altogether, therefore, the data indicate that there is another agent or agents constantly in operation whose effects are a large fraction of those obtained from temperature. These effects are overlaid upon that due to temperature and the sum of these is all that the measurements can show. The continual action of these agents is illustrated by the following data:

Time.	Potential Difference.	
10:30	+.945	
10:40	+.923	Inner cylinder of zinc.
10:52	+.928	Both cylinders at room temperature.
11:21	+.948	
11:38	+.946	

The first rapid lowering is the effect previously mentioned, that obtained when the inner cylinder is first brought out after standing in the outer for some time. This effect was found in all metals used and was sometimes as large as .065 volt in magnitude. That it was the result of standing inside the outer cylinder is evident because at any time while the potential was diminishing, the decrease could be checked or even reversed by letting the inner cylinder remain in the outer one for ten or fifteen minutes. After standing outside for some time the potential would reach a minimum and then go through some such variations as are given above, without any apparent regularity and from no evident cause. The cylinder merely stood in the air of a closed room illuminated by daylight and was not even approached.

It would seem then that the only way to get at the effect due to temperature alone would be to consider these extraneous effects as following the law of probability. The most nearly true value of the temperature effect would accordingly be reached by averaging. All observations on the variation of potential difference at constant temperature would tend to justify this method of interpretation, and it will accordingly be used. The curves appended give the results from most of the data obtained but certain effects peculiar to each metal will be mentioned here.

Copper.—Erskine-Murray found that copper if heated above 80° seemed to begin oxidizing or at least this was the action supposed to take place. It must be understood that it does not alter the appearance of the surface

in any noticeable way but the change is evidenced only by the fact that on cooling to room temperature the potential falls far below its value at the beginning. To assume that a slight oxidation has taken place seems the most reasonable explanation as oxidation of the surface will produce, a similar but larger effect. To locate the temperature at which this takes place in copper is somewhat difficult as in passing that point either when heating or cooling no marked change is to be noticed. It is determined only by the fact that if copper is heated above 80° its potential when cooled to room temperature again will be far below the value at the beginning, while if not heated to quite that temperature it will return practically to the original condition. The following data illustrate this action.

Potential Diff.	Temperature.	Potential Diff.	Temperature.
+.078	17.1	+.134	91.3
+.078	27.2	+.084	79.2
+.082	38.0	+.086	67.9
+.084	48.2	+.068	55.2
+.095	58.7	+.051	42.9
+.109	68.7	+.045	33.8
+.127	77.8	+.049	23.1
+.127	84.7		

Numerous trials located this oxidation point at closely 80°, the same as found by Erskine-Murray. The maximum temperature used in determining the true temperature effect is then always below 80°.

Zinc.—Zinc shows the same oxidation effect at 65° as copper does at 80° but it is much easier to locate the temperature at which the action begins. This is because at that point the potential begins to fall and increased temperature only increases the rate of fall. That this is not a change in the sign of the temperature coefficient is shown by the fact that in cooling the potential decreases continually and does not return through the values obtained in heating. In copper, it is evident that the temperature coefficient is greater than the effect of the oxidation and masks it so that the oxidation point can only be determined as described above. This point for zinc can be found from one measurement because of the sharp fall of potential when this temperature is exceedeed. The following data will illustrate this action and also how the change is a permanent one.

The rapid decrease shown in Part I. of these data is due to the oxidation effect minus the temperature effect and not to the sum of the two because Part II. shows that after the potential has been greatly decreased by overheating, the coefficient is still positive as for a normal zinc surface.

Erskine-Murray did not find this oxidation point because the maximum temperature he used with zinc was only 60°.

Potential Diff.	Temp.	Potential Diff.	Temp.
Part I. +.912	18.5	+.834	23.0
+.933	26.6	Part II. +.830	23.0
+.944	35.2	+.833	30.3
+.957	43.6	+.838	36.0
+.964	51.2	+.845	41.5
+.988	58.5	+.847	46.3
+.984	66.0	+.847	50.8
+.972	71.8	+.852	55.3
+.945	88.1	+.846	48.9
+.901	74.2	+.844	42.7
+.894	61.9	+.834	34.6
+.872	42.3	+.826	20.5
+.848	29.3		

For nickel, aluminum, and tin no temperature of oxidation was found up to the maximum used, 100°. Some of the observations on aluminum and tin might indicate otherwise but the lower potentials reached in these cases by cooling were only temporary effects. After standing for

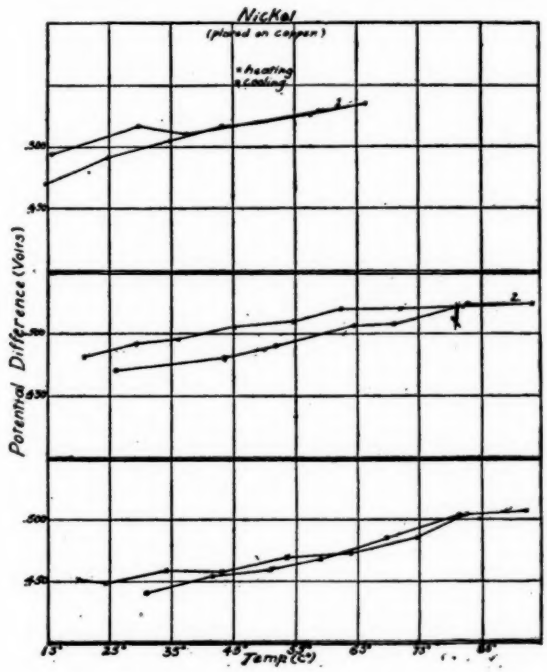

Fig. 3.

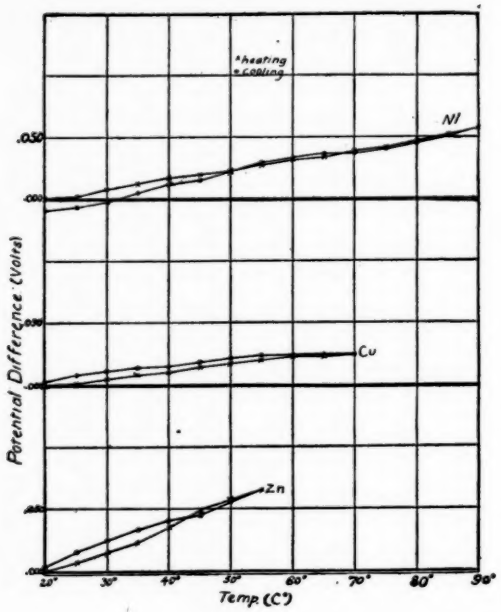
*heating
+cooling
Ni
Cu
Zn
.050
.000
.030
.00
.00
Potential Difference (Volts)
20°
30°
40°
50°
60°
70°
80°
90°
Temp. (C°)

Fig. 4.

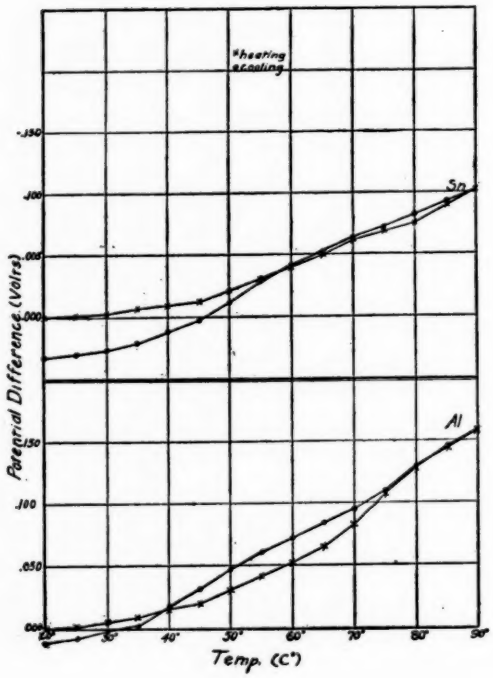
*heating
+cooling
Sn
Al
.150
.100
.005
.000
.150
.100
.050
.000
Potential Difference (Volts)
20°
30°
40°
50°
60°
70°
80°
90°
Temp. (C°)

Fig. 5.

an hour or so the potential in each of these cases rose to, or nearly to, the value before heating. This rise in potential was not a change due to temperature because the final temperature of an experiment was usually so nearly that of the room that the hour or more standing did not change it by more than one or two tenths of a degree.

It is to be noted here that Erskine-Murray is undoubtedly mistaken in the value he gives for the coefficient of tin as he found it to be negative while the data here given show tin to have one of the largest positive values.

Curves.—Fig. 3 contains the curves showing three sets of observations on nickel. These are given as being typical in every way of the observation curves for all the metals investigated. It was curves similar to these that were used in obtaining the average curves of Figs. 4 and 5 These figures show the average change in potential with temperature without any reference to the absolute value of the potential. The average curve for nickel (Fig. 4) was obtained by taking from curve 3, Fig. 3, the potential for every 5° from 20° up to the multiple of 5° nearest to the maximum temperature used for nickel. All these values of the potential were subtracted from the value at the highest temperature and the differences tabulated. Tabulations were made in the same way from curves 1 and 2 (Fig. 3). The three differences of potential for each temperature when heating were averaged and the three when cooling separately. The value of the potential on any curve that stopped short of this highest temperature used with nickel was obtained by extrapolation except where this would exceed 5°. Finally the zero of the plot was shifted to coincide with the potential on the average heating curve at 20° temperature. This procedure amounted to shifting vertically all the observation curves for nickel until the upper extremities coincided and then getting the average of the curves so placed, with attention given only to the change in potential. A similar process was carried out for each metal giving the curves of Figs. 4 and 5. No curve of these plates is the average of less than three observation curves.

This shifting to have the maximum points coincide instead of the initial points, or some others, was done because the heating and cooling curves, of necessity, coincide at this point but do not at any other. With this choice both the average heating and the average cooling curves for a metal could be referred to the one reference point and they would coincide at that point and would appear as the curves from a single set of observations. In a case such as shown for nickel where curve 1, Fig. 3, has a much shorter range than curves 2 and 3, the mean of these two was taken down to the highest temperature on curve 1. This curve was

then shifted until its extremity coincided with the mean of 2 and 3 at the same temperature. The average of the three curves was then used for the remaining lower temperatures.

Each curve of Fig. 6 is the average of the heating and cooling curves for each metal from Figs. 4 and 5. Then they are so shifted that the initial points of each resulting curve coincide with the potential which is the average of all the observed values of the difference in potential between each metal and the copper base.

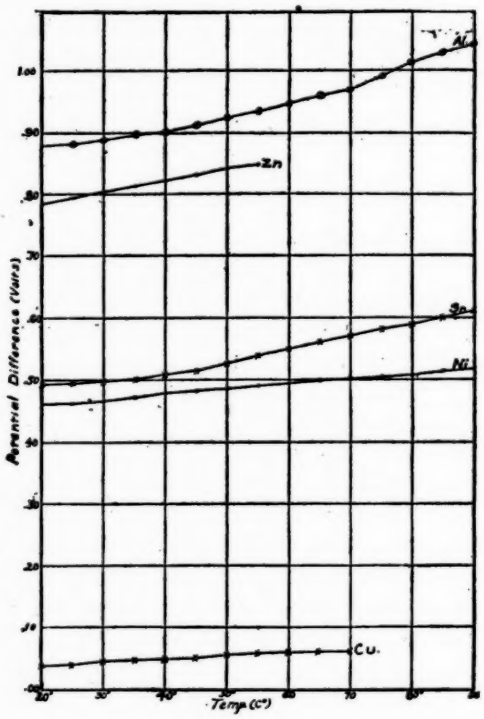

Fig. 6.

It appears that the curves for zinc, nickel, and copper are closely straight lines but those for tin and aluminum appear nearer an exponential form. The temperature coefficient for zinc, nickel, and copper is then constant over the whole range of temperature used, but for tin and aluminum it can be considered constant only for a limited range, as the numerical values below indicate.

Of course, only where the coefficient is constant would extrapolation be reasonable. Applying it to nickel, copper, and zinc, it was found that nickel and zinc would come to the same potential at − 242° (C.),

copper and zinc at − 371° (C.), and copper and nickel at − 1200° (C.). Erskine-Murray states that the curves he has given would intersect at about the absolute zero if extended, though how rough an approximation this is he does not mention. The above results do not agree with his statements, that is, they do not in the least indicate that all metals would come to the same potential at the absolute zero.

Metal.	Temp. Range.	Coefficient (Volts per Degree).
Copper	20° to 70°	.00050
Nickel	20° to 90°	.00086
Zinc	20° to 55°	.0024
Tin	20° to 45°	.00096
Tin	45° to 90°	.0020
Aluminum	20° to 40°	.0011
Aluminum	40° to 70°	.0023
Aluminum	70° to 90°	.0036

It might be presumed that all the above procedure of averaging was hardly permissible considering the wide divergence of the original data, but it was done on the assumption of one or more uncertain, extraneous effects being present. If, then, these follow the law of probability, that is, that the errors they introduce are as great and as often positive as negative, then the method of obtaining the results given is justified. It is recognized that the amount of data on some of the metals was rather meager to be handled in this way, but if the assumption of extraneous effects is correct, this method would give the most probable values of the measured quantities, no matter how few the observations. It is believed that the most reasonable method of consideration was used and that the data here presented offer some dependable values of the change of contact potential difference with temperature.

It is hoped later to give further data on other metals and perhaps with a wider range of temperature and also some other aspects of the subject may be considered at that time. In conclusion I wish to thank Professor Sanford and Professor Rogers for their interest in the problem and their timely advice throughout the experimental work.

STANFORD UNIVERSITY,
May, 1913.

NOTE ON POTENTIAL ATTAINED BY PHOTO-ELECTRIC CELLS IN DARKNESS.

BY J. W. WOODROW.

A FEW months ago, the present writer published in the PHYSICAL REVIEW[1] an account of experiments which seemed to show that strongly photo-electric metals liberated positive particles when kept in total darkness. These experiments were continued with the object of determining more definitely the exact nature of the charge obtained from the photo-electric metal in the preceding investigations. It was shown conclusively by the following methods that this charge was due to a "leak" across the surface of the glass insulation, from the potassium which will be at a positive potential with respect to the platinum electrode. First, a magnetic field, sufficiently strong to deflect positive ions away from the platinum electrode, had no effect whatsoever on the observed current. Then it was found that the current could be stopped by using an amber insulation in which was inserted a platinum guard-ring which protruded both inside and outside the walls of the photo-electric cell. In the previous experiments the guard-ring employed consisted merely of strips of earthed tinfoil wrapped about the glass walls, which was thus shown to be insufficient.

The increased current at the higher temperatures is probably due to two causes, the increased conductivity of the glass and the condensation of the vapor of the metal on the walls of the cell. S. H. Anderson[2] has also shown that with alternating fields applied to a photo-electric cell in darkness, there is no indication of the current one would expect if the metal liberated any kind of positive particles.

June, 1913.

[1] Vol. XXXV., p. 203, September, 1912.

[2] PHYS. REV., S. 2, Vol. I., p. 222, March, 1913.

THE PHOTOELECTRIC PROPERTIES AND CONTACT RESISTANCES OF THIN CATHODE FILMS.

BY OTTO STUHLMANN, JR., AND KARL T. COMPTON.

INTRODUCTION.

THE relation between the velocity of the electrons emitted by the action of light on metals and the frequency of the light was deduced by Einstein[1] on the unitary theory of light and was expressed by the equation

$$\tfrac{1}{2}mv^2 = eV = h\nu - w_0.$$

Here m is the mass, v the maximum velocity and e the charge of the electrons liberated by light of frequency ν. V is the difference of potential in electrostatic units, which is just sufficient to prevent these electrons from reaching the receiving electrode. h is Planck's constant and w_0 is the work done in the escape of an electron from the metal. Recently this same equation has been derived by Richardson[2] by thermodynamic and statistical methods which do not necessarily involve the unitary light hypothesis. Richardson's theory further enables the constant w_0 to be interpreted and calculated by the relation[3]

$$w_m - w_p = \frac{e}{300}\left\{ V_p - V_m - \theta\frac{\partial}{\partial\theta}(V_m - V_p)\right\},$$

where $w_m - w_p$ is the difference between the amounts of work required to liberate an electron from each of two metals m and p, and $V_p - V_m$ is the contact difference of potential, between the metals, expressed in volts. The last term, which expresses the Peltier effect, is so small in comparison with the contact difference of potential that it may be neglected in this work. w_0 has been measured directly for platinum[4] and for osmium[5] and is not far from $e/300\cdot5$ volts for platinum. From this value, w_0 for any other metal may be calculated from a knowledge of their contact differences of potential.

[1] Ann. der Physik, Vol. 17, p. 146 (1905).

[2] PHYS. REV., Vol. 34, p. 146 (1912); Phil. Mag., Vol. 23, p. 615 (1912); Science, Vol. 36, p. 57 (1912).

[3] Phil. Mag., Vol. 23, p. 620 (1912).

[4] O. W. Richardson, Phil. Trans., A, Vol. 201, p. 497 (1903); Vol. 207, p. 23 (1906). H. A. Wilson, Phil. Trans., A, Vol. 202, p. 243 (1903). F. Deininger, Ann. der Physik, Vol. 25, p. 396 (1908). O. W. Richardson and H. L. Cooke, Phil. Mag., Vol. 20, p. 173 (1910).

[5] H. L. Cooke and O. W. Richardson, PHYS. REV., Series 2, Vol. 1, p. 71 (1913).

These relations have been tested[1] for a large number of different metals and frequencies, and have been found to be consistent with the experimental results, within the probable limits of accuracy of the experimental methods employed.

Several investigators have succeeded in obtaining electron velocities considerably higher than those ordinarily obtained in photoelectric measurements. Most of these high velocities have been obtained when sparks were used as the source of light. These have been shown to be due to secondary action from electro-magnetic radiation accompanying the spark discharge. However high velocities have also been obtained in other ways. Von Baeyer and Gehrts[2] obtained velocities equivalent to 6.3 volts for electrons from copper, gold and aluminium after passing an induction coil discharge between the emitting and receiving electrodes. Recently Dike[3] has published results of experiments in which he obtained values of the maximum initial kinetic energy equivalent to as much as 44 volts for electrons liberated from thin platinum cathode films when illuminated by light from a quartz mercury arc. These results were repeated by Dike and Brown,[4] who obtained values as large as 52 volts under conditions similar to those in Dike's first experiment.

It is evident that if these results are correct they render Richardson's theory untenable. From the relation $V = 300/e \cdot (h\nu - w_0)$ discussed above, we may calculate the maximum potential possible according to the theory. 180 $\mu\mu$ is the shortest wave-length of light that will pass through the air and quartz interposed between the source of light and the illuminated metal. Take w_0 for platinum to be approximately 5 volts. Substituting these values in the above equation we find $V = 1.95$ volts. Even if the work done on an electron in escaping from the metal were zero we would still have V equal to only 9.95 volts. This is the upper limit allowed to any substance by Richardson's theory. It is an impossibly favorable case but it still falls far short of explaining the high velocities found by Dike.

It seems necessary, then, either to reject Richardson's theory or to discover some error in the results or the interpretation of the results given by Dike. It was with the purpose of discovering whether these high velocities are real or only apparent photoelectric velocities that we undertook this investigation.

[1] Richardson and Compton, Phil. Mag., Vol. 24, p. 575 (1912); A. L. Hughes, Phil. Trans., A, Vol. 212, p. 205 (1912).

[2] Ber. d. D. Phys. Gesell., Vol. 21, p. 870 (1910).

[3] PHYS. REV., Vol. 34, p. 459 (1912).

[4] PHYS. REV., Series 2, Vol. 1, p. 254 (1913).

One of the writers[1] has shown that the velocity actually measured in photoelectric experiments consists of two parts, (1) the true initial velocity with which the electrons are liberated and (2) a velocity acquired after emission due to the force exerted on the electrons, arising from the contact difference of potential between the emitting and receiving electrodes. Of these two parts, only (1) has anything to do with the photoelectric effect and it is only this part of the measured potential which should be considered as due to photoelectric action. It seemed probable that the great increase in the photoelectric potentials following an induction coil discharge might be due principally or entirely to a great increase in the contact difference of potential. Thus the initial kinetic energy with which the electrons leave the metal film may have the ordinary value predicted by Richardson's theory. But after emission this velocity may be greatly increased by the repulsion due to an absorbed negative charge in the sputtered plate or due to their passage through a charged insulating layer, deposited on the surface by the induction coil discharge. With the object in view of testing these explanations of the apparent high velocities, these experiments were undertaken.

APPARATUS.

Our apparatus, shown in Fig. 1, is essentially the same in size and arrangement as that used by Dike,[2] with the addition of an arrangement for testing the contact difference of potential between the emitting

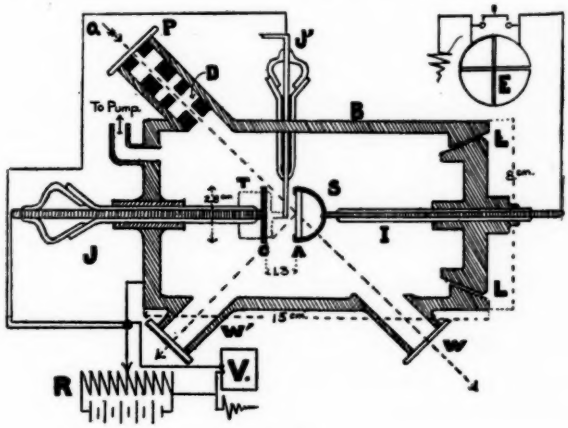

Fig. 1.

electrode and the surrounding vessel. *BB* is a cylindrical brass vessel 15 cm. long and 8 cm. in diameter. It is closed at one end by an accu-

[1] K. T. Compton, Phil. Mag., Vol. 23, p. 579 (1912).

[2] PHYS. REV., Vol. 34, p. 465 (1912).

rately turned and ground lid, and wax could be poured into the grooves *LL* to render the vessel airtight. Through this lid extends an insulated rod *I*, which carries on its end a stirrup *S*, supporting the plate *A* on which the film under investigation is to be deposited and tested. This plate is about 2 cm. square and is connected to an electrometer *E* giving a deflection of 180 divisions per volt at a scale distance of one meter. The films were sputtered on the plate *A* from a platinum cathode *C*, which, when not in use, could be turned out of the way by rotating the ground glass joint *J* through half a revolution.

Light from a quartz mercury arc *Q* entered the vessel through a quartz window *P* and a side tube provided with diaphragms *D*. When a quartz plate was in position at *A* the transmitted light passed out of the vessel through a window *W*, and the reflected light escaped through *W'*. In this way the reverse stream of electrons due to light incident upon the sides of the vessel was practically eliminated. The vessel could be charged to any desired potential from a potentiometer circuit *R*. The maximum initial kinetic energies of the electrons, expressed in equivalent volts, were determined by charging the vessel to such a negative potential that the electrometer showed no deflection. The voltmeter *V* then gave the maximum potential directly. By this *null* method we avoided possible errors due to faulty insulation. When saturation currents were to be measured, the vessel was charged to a sufficiently high positive potential and the rate of deflection of the electrometer noted.

As pointed out above, it is necessary to apply a correction for contact difference of potential to the measured values of the maximum potential in order to find the true photoelecrtic potentials. This contact difference of potential between the metal film on *A* and the vessel *BB* was determined by the Kelvin method.[1] The contact difference of potential tester *T* consisted of a brass plate, of the same dimensions as the plate *A*, fixed on a movable arm to the end of a brass rod which extended to the outside of the vessel through the ground glass joint *J'*. By rotating this joint the test plate could be moved close to *A* or back against the side of the vessel. The tester *T* was raised to various potentials from the divided circuit *R*, and the potential was so adjusted that no kick of the electrometer was produced by moving *T* back and forth in front of *A*. The voltmeter, under these conditions, gave a direct measure of the contact difference of potential between *T* and *A*. An objection to this arrangement is that it measures the contact difference of potential between the emitting electrode and *only a particular part* of the receiving electrode. If the inside of the vessel always remains a polished brass

[1] Kelvin, Phil. Mag., Vol. 56, p. 82 (1898).

surface this arrangement would introduce no error. However, if the induction coil discharge, during the process of sputtering, changes the condition of the inside surface of the vessel and changes it more in some regions than in others, the above method will not be accurate, because it is not certain that the contact difference of potential actually measured is the true difference of potential between the emitting electrode and that portion of the vessel to which most of the electrons are escaping. Nevertheless, if any considerable changes in the contact difference of potential occur, this method should give at least an approximate measure of these changes. For this reason the contact potential measurements should be considered as indications of what surface changes are produced by the electrical discharge rather than as accurate quantitative measures of these changes. It will be seen, however, that these indications are fairly accurate, especially in the case of the larger effects measured.

The sputtering was all done at a pressure of $(10)^{-4}$ cm. of mercury by means of the discharge from a small induction coil capable of giving a spark of about 4 cm. in air. The thickness of the deposited film may be taken to be proportional to the time of sputtering. The photoelectric measurements were all made at a pressure of $5(10)^{-6}$ cm. or less.

Effect of Reflected Electrons.

A number of investigators[1] have assumed that electronic reflection at the receiving electrode causes a reverse stream of electrons which reduces the measured value of the maximum acquired photoelectric potential. Dike and Brown[2] offered this as one of the possible reasons for the high potentials obtained in their experiments. They further suggested that Robinson,[3] who also worked with sputtered films, did not obtain high velocities like they did because the construction of his apparatus may have made a difference in the amount of electronic reflection. It is hard to see, however, how electron reflection can have any effect on the maximum photoelectric potential. Suppose that fifty per cent. of the fastest electrons which strike the receiving electrode are reflected and return to the plate from which they started. This will not prevent the electrode from charging to the same maximum potential which it would attain were there no reflection. Under these conditions the final potential will be attained just half as rapidly, but it is inconceivable that the final potential will be altered. Especially is this true when the maximum potential is measured by a *null* method which eliminates errors

[1] Ladenburg and Markau, Verh. d. D. Phys. Ges., p. 562 (1908); Von Baeyer and Gehrts, loc. cit.; Klages, Ann. der Phys., Vol. 31, p. 343 (1910).

[2] PHYS. REV., Series 2, Vol. 1, p. 254 (1913).

[3] Phil. Mag., Vol. 23, p. 542 (1912).

due to imperfect insulation. Electronic reflection certainly must be prevented in case "distribution of velocity" curves are to be obtained, but its influence may be neglected in measurements of maximum potentials or of saturation currents. The apparent increase in the maximum potentials when electron reflection has been reduced by a perforated gauze and an auxiliary field has been shown to be a spurious effect.[1] For these reasons we have, in these measurements, made no effort to measure or prevent electronic reflection.

ORDINARY PHOTOELECTRIC POTENTIALS.

(*a*) *No Evidence of Absorbed Charge.*—In our first trials the cathode films were deposited on quartz in a separate sputtering vessel, which consisted of a large glass bell-jar waxed on a brass base plate, with the electrodes sealed in. The contact difference of potential was then tested in air by the ionization method,[2] which is more accurate than the Kelvin method but which may only be used while the films are in contact with the air. Then the sputtered plate was placed in position in the apparatus, the vessel exhausted and the maximum photoelectric potential measured. This process was repeated for three films of different thicknesses. The results are shown in Table I.

TABLE I.

Potential.	Platinum Film.		
	Very Thin.	Medium.	Thick.
Maximum	1.45 volts	1.65 volts	1.85 volts
Contact	−0.15	−0.15	−0.15
Corrected	1.30	1.50	1.70

Evidently this method does not yield the high potentials found by other investigators. On the other hand these maximum potentials are of the order of magnitude predicted by Richardson's theory. While the potential apparently is higher for the thicker films, the differences are small and may be due to experimental error, since the apparatus is not well designed for measuring potentials accurately to a fraction of a volt.

The results are, however, of some interest. The contact differences of potential are practically identical with that between brass and ordinary platinum. The photoelectric potentials are also what one might expect from platinum foil. It is quite certain, therefore, that these films consist of true platinum. The photoelectric potentials showed a

[1] Compton, Phil. Mag., Vol. 23, p. 277 (1912).

[2] Kelvin, Beattie and Smolan, Phil. Mag., Vol. 45, p. 277 (1898).

tendency to increase slightly with time, the increase amounting to one or two tenths of a volt in several hours. This "aging" effect has been noticed before by Dike and by one of the writers.[1] The saturation currents were larger than those usually obtained from platinum. This was true for all the sputtered films investigated. An important result bearing on the problem under investigation is that the induction coil

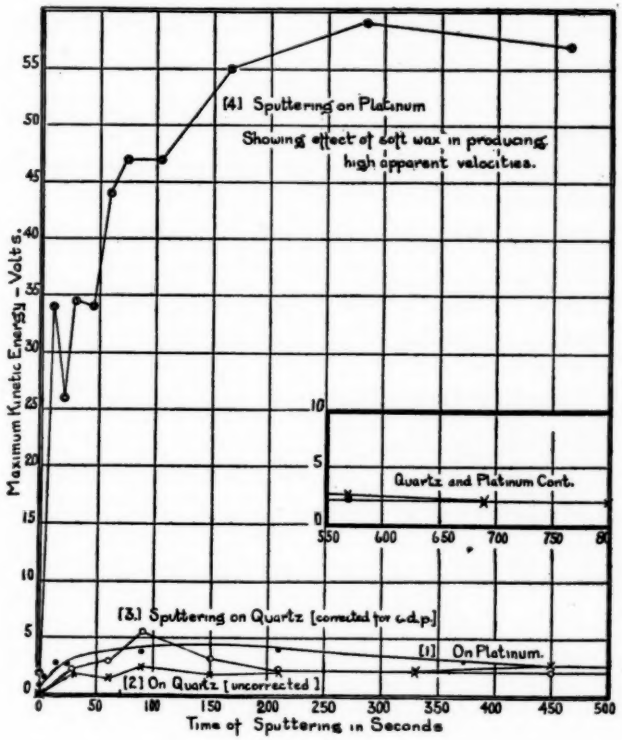
[4] Sputtering on Platinum
Showing effect of soft wax in producing high apparent velocities.
Quartz and Platinum Cont.
[3.] Sputtering on Quartz [corrected for c.d.p.]
[1] On Platinum.
[2] On Quartz [uncorrected]
Maximum Kinetic Energy - Volts.
Time of Sputtering in Seconds

Fig. 2.

discharge evidently produces no "absorbed" charge in the quartz. Hence the high potentials obtained by Dike cannot be ascribed to this cause. An absorbed charge in the quartz, if it existed, would not have vanished immediately on contact with the air and would have been easily detected by the contact difference of potential measurements.

(*b*) *Films Sputtered and Investigated in Vacuo.*—Films sputtered on quartz and on platinum foil in the apparatus (Fig. 1) were tested for contact difference of potential and for photoelectric potentials and saturation currents without allowing the films to come in contact with the air.

[1] Stuhlmann, PHYS. REV., Series 2, Vol. 4, p. 330 (1913).

Results as shown in Fig. 2, curves 1, 2 and 3, were obtained. Curve 1 represents the variation of maximum potential with the time of sputtering, for films sputtered on a platinum plate. The highest measured potential is 3.9 volts. Since the contact difference of potential remained too small to be detected accurately by the Kelvin method no corrections for contact difference of potential were made. Curve 2 represents the photoelectric potentials for various thicknesses of films deposited on quartz. In this case the contact differences of potential were measurable and the corrected potentials are shown in curve 3.

Several facts are evident from these results. The potentials were rather irregular, most of the irregularities occurring in the early stages of sputtering. The contact differences of potential also varied, and further experiments showed that they varied also in different parts of the vessel. These photoelectric potentials are distinctly higher than those for ordinary platinum, although they still fall far short of those obtained by Dike and Brown.[1] Since the following experiment throws light on these results they will not be discussed further at this point.

SPURIOUS HIGH PHOTOELECTRIC POTENTIALS.

Up to this point it appeared that, although we had followed closely the method used by Dike, we were unable to duplicate his high velocities. Following a suggestion from Professor Richardson, however, we made another trial and succeeded in obtaining the high potentials, even exceeding the highest values obtained by either Dike or Brown.

TABLE II.

Time Sputtered.	Contact Potential.	Photoelectric Potential.
0 sec.	− 0.1 volt	1.8 volt
10	−16	35
10	−22	26
10	−28	34.5
15	−28	34
15	−37	44
15	−40.5	47
30	−40	47
60	−57	55
120	−57	59
180	−57	57

A tiny bit of soft wax was placed on the sputtering cathode and the above experiments were repeated. From the first the measured potentials were high, and are here shown graphically in Fig. 2, curve 4. After

[1] Loc. cit.

a film due to five minutes of sputtering had been deposited the corresponding maximum observed potential had risen to 59 volts. Further sputtering did not increase this value.

That these high potentials do not indicate high photoelectric velocities is shown by the fact that the contact difference of potential between the film and the vessel increased parallel with the photoelectric potential, in such a direction as to make the emitting film electro-negative and repel the electrons after they were emitted. The parallelism between these quantities is shown in Table II.

This enormous contact difference of potential is not the true contact difference of potential between the film and the chamber of the apparatus. If these high values represented true contact differences of potential, no photoelectric effect would be possible with light of the frequency used, since under these conditions $h\nu$ would be smaller than w_0. The effect is evidently due to a charged layer of soft wax covering the platinum film, within which layer the escaping electrons experience an enormous acceleration. This charged layer persisted for about 24 hours after air had been let into the apparatus. During this time the apparent contact difference of potential gradually fell to its normal value of $-$ 0.15 volt. The saturation currents under these conditions were a little more than half as large as in the similar tests where the soft wax had been omitted. This again gives evidence of some sort of layer through which the electrons were obliged to pass while escaping.

It is evident from these results that the high potentials observed by Dike and later also by Dike and Brown must be ascribed to the presence of oil or grease introduced while making the metal apparatus, to vacuum wax in the ground joints or to some other material which could produce such layers as suggested. Doubtless the small increase in potential which we observed before we intentionally introduced the soft wax was due to wax or grease unavoidably present in any form of metal apparatus.

There is therefore no evidence in these experiments to show that the photoelectric velocities should be different from those predicted by Richardson's theory. There are certain theoretical reasons for believing in the possibility of small variations in the saturation currents and maximum potentials from very thin films; but these effects, if they exist, will probably not exceed a fraction of a volt and will be taken into account by a variation in the quantity w_0 for very thin films.

Saturation Currents and Contact Resistances.

Several interesting phenomena are exhibited by the relations between saturation photoelectric currents and thickness of films, which are shown graphically in Fig. 3.

One of the most striking things about these curves is the influence of the nature of the contacts on the shape of the curves. In curve 5 the film was deposited directly on a platinum plate. The saturation curve under these conditions is a smooth curve of logarithmic form. Contact between the sputtered film and the platinum plate was evidently established from the very beginning, as is indicated by the lack of certain characteristic phenomena which appear in all curves for saturation

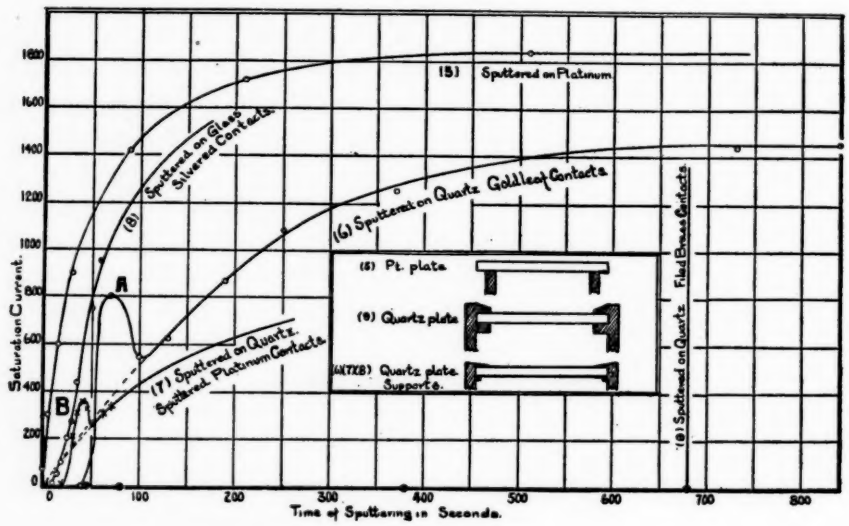

Fig. 3.

currents from films sputtered on glass or quartz. In curve 7 the contact between the sputtered film and the supporting stirrup was made as follows. A thick opaque platinum film was first sputtered on the quartz and a central strip was removed, leaving two strips of film about 3 mm. wide on the two opposite edges. The clamps of the stirrup were now fastened to these edgings and the films to be investigated were sputtered over this prepared surface. This was done with the idea in view that the film to be deposited would spread in a uniform layer over the cleaned quartz and the sputtered contacts alike, and in this way the preliminary film would serve as an intermediate contact between the sputtered film and the contact clamp. It is evident in this case that contact was not perfect from the beginning as in the case of curve 5, and that no contact with the film was established until the sputtering had continued about 25 seconds.

To show that the absence of photoelectric currents in the early stages of sputtering is really due to the absence of electrical contact rather than

to some inherent photoelectric property of very thin films, various other methods of making contact were employed. These methods, with their differences greatly exaggerated, are shown in Fig. 3. For curve 6 we used gold leaf contacts. Strips of gold leaf were placed firmly adhering to the two opposite edges of the quartz plate and the contacts were clamped down on this leaf. In this case the discontinuity of surface between the quartz and the gold leaf would be more pronounced than between the quartz and the sputtered film used previously. The preliminary film used for contact in the case of curve 7 was much thinner than the gold leaf and therefore a less abrupt discontinuity was found between the film under investigation and the contacts. As might be expected, the contact in this case was more difficult to establish, and was not obtained until the sputtering had continued for about 55 seconds.

A still greater degree of difficulty in establishing contact between film and holder is shown by curve 9. In this case a clean quartz plate was simply held in a brass clamp whose edges had been filed down to a very sharp angle, whose vertex rested flush on the quartz plate. The bounding surface was much more abrupt in this case than in the others. This time sputtering continued for at least 680 seconds before contact was made and currents obtained from the film. In fact this film was of such a thickness as to be quite opaque.

It is evidently a very difficult matter to make good electrical contact with very thin films. The less abrupt the boundary between the surface of the contact film or plate and the quartz surface on which the film is deposited, the more perfect will be the contact. At first sight it may seem unlikely that a contact edge as thin as gold leaf would prevent uniform deposition and perfect contact with the film. But when one remembers that these thinnest films are many times thinner than a wave-length of light, it is easy to believe that the deposited molecules must "bank up," so to speak, at the edge of the contact before continuity is obtained.

There are two applications of this experiment on the effect of the method of making contact with the films, to which we would call attention. In the first place it explains why, in our results and also in the recent results of Robinson,[1] little or no photoelectric current was observed until the film had reached a certain thickness, where the current showed a sudden increase. The above results seem to show that this is due to imperfect contact rather than to any inherent property of very thin films.

It also offers a possible explanation of some of the results obtained by

[1] Phil. Mag., Vol. 25, p. 115 (1913).

Patterson[1] on the specific resistance of thin metal films. He found for very thin platinum films that the specific resistance increased more rapidly than was predicted by the electron theory of conduction suggested by J. J. Thomson.[2] It seems possible that all or part of this unpredicted increase may be due to high contact resistance superposed on the regular resistance of the film. If this is true it would explain the discrepancy between theory and experiment in the case of very thin films. We also tested photoelectrically a film with contacts very similar to those used by Patterson, with the results shown in curve 8. The contact between film and holder was here established by sputtering the platinum film over a quartz plate whose two opposite edges had been covered by means of a semitransparent silver film, deposited by the Rochelle salt method. This method of establishing electrical contact between film and holder was evidently the most perfect yet tried. As seen from the curve, contact was established soon after 10 seconds' deposition. Had contact been made from the first it is probable that the resistance which Patterson measured would have been found to conform more closely to the theory discussed in his paper.

[1] Phil. Mag., Vol. 4, p. 652 (1902).
[2] Proc. Camb. Phil. Soc., Vol. 11, 2, p. 119 (1901).

VECTOR POTENTIAL IN RELATION TO VECTOR ANGLE

BY FREDERICK SLATE.

THE recent freer use of the various potentials has not carried with it their adoption as quantities that are physical in the fullest sense of the word; they continue to be set off somewhat as "Rechnungsgrössen"—formal aids to calculation or summarized expression, employed without always searching deep for possible physical significance. It is true that the oldest potential, the scalar potential of gravitation, electric charges and magnets, has recognized connections with energy, familiar enough in fact to guide the conventions standardizing its sign and magnitude. But the vector potential, its chief companion, is still more enveloped in mathematical haze than is desirable; its physical aspects are obscured by its association with certain operations and theorems whose mystery is not yet dissipated. As a mode of statement within modern electromagnetic theory, however, accepted finally, it would appear, after some protest against its inadequacy or superfluousness, the vector potential will be engaging increased attention. It should be properly strengthened by whatever of direct physical meaning we can gather round it, and what follows here is a small contribution to that general end, taking up a clew offered through the vector algebra, which enables us to read a new sense into the parallelism between the scalar and the vector potential, to the advantage of the latter, rated as a physical concept.

First as to the geometrical and preparatory ideas, that happen to be connected with solid angle. Assuming a pole (P) let the extremity of a radius vector ($\boldsymbol{r}$) be guided along any closed curve (s) in space, tracing in general some conical mantle, whose surface we may suppose not to cut itself, in order to avoid mere complication in details. Then the differential tangent-sectors give instantaneously the resultant elements of plane angle described by the radius vector, the aggregate of angle being a vector sum. This appears in the form

$$d\boldsymbol{a}_1 = \frac{\mathbf{I}}{r^2}[\boldsymbol{r}d\boldsymbol{s}]; \int d\boldsymbol{a}_1 = \int_s \frac{\mathbf{I}}{r^2}[\boldsymbol{r}d\boldsymbol{s}], \qquad (1)$$

which includes the particular case where the guide-curve (s) lies all in one plane that contains the pole (P) also.[1] The sphere of unit radius

[1] Slate, PHYS. REV., N. S., *1*, p. 56.

(unit sphere) centered at the pole determines by its intersection with the conical mantle the boundary (s_1) of the solid angle subtended by the curve (s) at the point (P), if we accept the area of the spherical cap ($r = 1$) as the measure of that solid angle.[1] Then by a simple continuation we write the vector expression for an areal element on the unit sphere, in the strip bordered by the curve (s_1) whose width is determined by a second coördinate ($d\boldsymbol{s}_2$),

$$d\boldsymbol{S}_1 = [d\boldsymbol{s}_1 d\boldsymbol{s}_2] = [d\boldsymbol{a}_1 d\boldsymbol{a}_2]. \qquad (2)$$

The third member of this equation can be read in two ways, according to the form of the thought attached to the second member. First, in terms of angle-area, the third member multiplies axial vectors; perpendiculars to the linear vectors multiplied in the second member, but numerically equal, each to each. The second factor ($d\boldsymbol{a}_2$) is the angle for the center (P) corresponding to the arc ($d\boldsymbol{s}_2$). The product, being of necessity oriented in the radius vector, is evidently unchanged by turning both factors through any common angle about that line. But secondly, the factors in the third member are only synonyms for those in the second, if we can adopt the arc-element of the unit circle to represent angle (*i. e.*, by a linear vector in the plane of the angle).[2] Either point of view enables us to look upon solid angle as generated by an integrated double movement in plane angle of the radius vector, a scalar sum being formed finally of the elements of area whose normals are all radial. And since the cap has been taken on the unit sphere, these results again are entirely consistent with a connection of solid angle and volume, through the expression[3]

$$A = \int_S \frac{1}{r^3}(\boldsymbol{r} d\boldsymbol{S}). \qquad (3)$$

Further, as a closing word on the geometrical relations, we may note that the sector of the unit sphere determined by the curve (s_1) being

[1] Following Maxwell's definition, El. and Mag., *2*, p. 39. A double or triple line of specification, whose equivalences rest finally upon certain coincidences of value for unit radius, is found current and supported by good authority through the whole group of angular quantities. There seems to be no ground in logic for adhering exclusively to one plan and ignoring special conveniences; and any necessary reassignment of dimensions can be taken account of easily. This freedom of choice among alternatives is made use of later.

[2] This presentation of angle as arc-element is not complete in vector algebra, it is clear, unless somehow supplemented by knowledge of the angle's plane; here, *e. g.*, through location of the center (P). This measure of angle underlies the specification of angular velocity as cm./sec. (explicit in Klein and Sommerfeld, Kreiseltheorie, p. 11). Such instances remind us that a vector quantity may be treated on more conventional bases than one; with "no questions asked" about pedigree.

[3] Slate, loc. cit., p. 57.

bounded by a closed surface, the projections on any plane of its conical mantle and of its spherical cap must be equal magnitudes, but subject in sign, of course, to the established rule of "outward normal." This conclusion has an evident extension to any distribution of physical vector that is homogeneously proportional to area throughout mantle and cap.[1]

Passing now to physical application of what precedes, as a matter of greater present concern, the most essential points can be brought out if we consider the simplest case: The curve (s) is a rigid conducting circuit carrying stationary current, and a positive magnet-pole is at the point (P). The inclusion of displacement current; and of conditions that introduce retarded potentials; can be shown without difficulty to demand no fundamental modifications. Reckoning then for unit of current and of pole strength (and we will add unit of permeability), the resultant interaction between the pole and a current-element in the direction $(d\boldsymbol{s})$ at an angle (ϑ) with the radius vector $(\boldsymbol{r})$ drawn from the point (P), is given correctly by

$$d\boldsymbol{F}_1 = \pm \frac{\mathrm{I}}{r^3}[\boldsymbol{r}d\boldsymbol{s}]. \tag{4}$$

For our purpose the relations depend upon configuration, and we may regard the pole as fixed, while the circuit suffers translational displacement. The element of force-moment for origin at (P), active on the element of circuit, is

$$d\boldsymbol{M}_1 = \left[\boldsymbol{r}, -\frac{\mathrm{I}}{r^3}[\boldsymbol{r}d\boldsymbol{s}]\right] = d\boldsymbol{s}_1 = \frac{ds}{r}\sin\vartheta \left\{ \begin{array}{l} \text{perpendicular to } \boldsymbol{r} \\ \text{in the plane } (\boldsymbol{r}, d\boldsymbol{s}) \end{array} \right\}. \tag{5}$$

The directed elements of the curve (s_1) on the unit sphere gain thus a new special meaning, adaptable to any general values for current and pole-strength by the introduction of a proper tensor as factor, which we shall continue here, however, to treat as unity. Moreover, our value for the element of force-moment about an axis at (P) drawn parallel to $(d\boldsymbol{s}_1)$ exhibits to inspection a maximum (all other conditions remaining unaltered),

$$d\boldsymbol{M}_1(\text{max.}) \equiv d\boldsymbol{M} = \frac{\mathrm{I}}{r}d\boldsymbol{s}\left[\text{for the direction } \vartheta = \frac{\pi}{2}\right]. \tag{6}$$

And the form of the expression in eq. (5) opens the way to consider this maximum (oriented parallel to $(d\boldsymbol{s})$) as a resultant, in the sense that its projection upon the actual axis yields the force-moment available about

[1] Compare Maxwell, El. and Mag., 2, pp. 29–44, as a classic reference, needing only to be "popularized" by translation into simpler modern forms, and by some reading between the lines.

that axis. Therefore specially, assuming reference axes at the origin (P) and using the direction-cosines (l, m, n) of ($d\boldsymbol{s}$), we derive for moments available about (X, Y, Z):

$$dM_x = \frac{l}{r}ds;\ dM_y = \frac{m}{r}ds;\ dM_z = \frac{n}{r}ds. \tag{7}$$

Let now the circuit (s) be shifted by translation, causing angular displacement ($d\boldsymbol{a}$) of the radius vector drawn to ($d\boldsymbol{s}$), and the doing of work by the force-moment ($d\boldsymbol{M}_1$) to the amount

$$dW = (d\boldsymbol{M}_1 d\boldsymbol{a}) = d\boldsymbol{M}_1 d\boldsymbol{a}' = (d\boldsymbol{M} d\boldsymbol{a}'). \tag{8}$$

The factor ($d\boldsymbol{a}'$) is the effective angular displacement; namely the component colinear with the total force-moment ($d\boldsymbol{M}_1$) of eq. (5). Hence we may read equations (7) and (8) in these terms:

The maximum force-moment ($d\boldsymbol{M}$) gives by a definite plan of projection upon any line through the origin the work per unit angle (or also the work reckoned for unit angle) of displacement about that line as axis. And these alternatives are dimensionally equivalent, when angle is a numerical quantity.

And further, returning to eq. (2), since the factors ($d\boldsymbol{s}_1$) and ($d\boldsymbol{a}_2$) are colinear when the width ($d\boldsymbol{s}_2$) is perpendicular to ($d\boldsymbol{s}_1$) and we are dealing with angle-area, the scalar product in eq. (8) is the numerical equivalent of the vector product in eq. (2); and on comparing we can see how the work done locally by the active moment comes to be measurable by an increment ($d\boldsymbol{S}_1$) of solid angle at an element of the boundary (s_1).

But it may be desirable to think of the pole as displaceable and the circuit as fixed; and this transition offers no difficulty. For just as both aspects of an interaction in the junction-line of two active elements are comprehended in one concept of stress, so an interaction of the present type that is perpendicular to the line joining the active elements may be viewed inclusively as one couple, whose moment-vector accordingly may be drawn indifferently at either end of the radius vector. And the same work-element also is determined from each point of view, because the angular displacement retains sign and magnitude, when adjusted to the equivalent linear displacements of pole and circuit, which must be opposite as well as equal.

The attention given thus far to the differential element only of the interaction between circuit and pole does in fact reveal all the essentials of the situation. But it remains necessary to express the result of summing effects by taking account of the whole group of elements in the circuit (s). We can execute this conveniently by forming from eq. (7) the algebraic integrals

$$M_x = \int_s \frac{l}{r} ds;\ M_y = \int_s \frac{m}{r} ds;\ M_z = \int_s \frac{n}{r} ds. \tag{9}$$

These expressions for its components enable us to recognize the quantity $\boldsymbol{M} = \boldsymbol{M}_x + \boldsymbol{M}_y + \boldsymbol{M}_z$ as the vector potential at the point (P); and the same identification is deduced from eq. (6), if we write for the vector sum and its components[1]

$$\boldsymbol{M} = \int_s d\boldsymbol{M};\ M_x = M\cos\alpha;\ M_y = M\cos\beta;\ M_z = M\cos\gamma. \tag{10}$$

It is apparent that no important difference exists between the two statements; only an interchanged order of the operations: (1) Projection; and (2) summation; plainly justified by the fundamental equivalence of resultant and its group of components as affected by the same operator. We shall note this legitimate inversion in another connection presently. The main result of our discussion might then be summarized at this stage in a definition of vector potential as a single-valued vector point-function, whose local value is determined in direction and magnitude by the total at each point of the force-moments due to other active material in the field, and described in the italics following eq. (8). We are thus put in a position to anticipate the reason why the vector potential presents itself as a convenience, where (and wherever) the field-forces, though (1) functions of the relative coördinates only, are (2) perpendicular to junction-lines and not directed along them; and how the scalar and the vector potential are supplementary in the dynamics of force-fields; primarily, we may say, as regards the types of interaction to which they apply naturally, for their equality in dimensions (those of energy) is on the surface formal and will not lead far. Nevertheless, the formulation in the above terms suggests on another side a comparison of the vector potential with the vector parameter (gradient) of the scalar potential rather than direct association of the potentials themselves. For the gradient may be specified in complete parallel, by substituting the element of (radial) force for the element of force-moment in the vector

[1] Eq. (9) is the plain equivalent of Maxwell, El. and Mag., 2, p. 44, eq. (9); while his construction (p. 44, foot) can be based directly upon our eq. (10), which is also (for unit of current) the vector form found in the literature of electromagnetism. It is worth remarking that this type of line-integral shows the aggregate effect of some actual and limited distribution *in situ;* for instance, the total weight of a curved rope, not uniform in cross-section. To repeat such a summation would be meaningless, whereas a progressive displacement round a closed curve is capable of repetition, and may give through a line-integral work corresponding to a multiple-valued potential. Observe further that the integrals of eq. (9) may possibly vanish as moments, though the summed work of the moment-elements does not become zero. This is a counterpart of the fact that a couple (which is zero force) may contribute a finite amount of work.

potential. That is, with inversion of the more habitual process, just quoted as allowable, the gradient too can be obtained by assembling the projections of a group of elementary force-maxima. Pairing in the way indicated, the distribution of forcive throughout the field can be traced; the local value of the vector potential yields force-moment, and that of the gradient yields force; in both cases alike by the one operation of projection. It is equally true, however, as another unconstrained reading of what precedes, that the force-moment about any line is obtainable by a process akin to "axial differentiation" with respect to vector-angle applied to the vector potential; leading here to the same result as mere projection because this particular differentiation leaves dimensions unaltered when angle is a ratio.

If the vector potential gives one method of expressing work, known to be energetically equivalent to a second method where the scalar potential is used, the same amount of work for any given displacement becomes calculable in terms of force-moment exerted during a turning and also in terms of linear displacement under a straight pull. The familiar connection between a current-circuit and a properly chosen magnetic shell is readily deducible on the basis of eq. (8), the values of the potentials being harmonized by taking the conventional zero at infinity for both. But we must expect that an attempt to develop complete symmetry in the operations applied to the two potentials and their results will be disturbed by obstacles. For example, the imperfect balance of cross relations between forces and couples prevents a match to the partial determination of moment by the former with a contribution to force by the latter; couple-moments are free vectors while a force vector may be localized in its "line of action." Again the junction-line of two active elements is unique, but a coördinate perpendicular to such a line needs further definition. Consequently, when a derivative of the vector potential is connected with a force perpendicular to the coördinate used in forming the derivative, the particular perpendicular is in fact also specified. This is perhaps the closest analysis of the necessary vector quality in this potential; and it underlies as well the occurrence here of the curl operator, as causing "quadrantal advance" in direction for the derivatives that enter.

UNIVERSITY OF CALIFORNIA.

THERMAL AND ELECTRICAL CONDUCTIVITIES OF THE ALKALI METALS.

By J. W. Hornbeck.

I. Introduction.

ONE of the first successes of the modern electron theory consisted in its very simple explanation of the constant ratio of the thermal and electrical conductivities for the metallic elements. However, a closer study of the conduction of heat and electricity through metals, of their thermo-electric and magnetic properties, showed that the simple theory, which considered the electrons to move freely through the metal, was unable to explain the manifold and complicated phenomena in a satisfactory way.

It was first assumed, in the theories of Riecke, Drude, J. J. Thomson and H. A. Lorentz, that the electrons are free and share the heat motion of the atoms; but this assumption leads to a number of contradictions. When one determines N, the number of free electrons per cubic centimeter, by the method of the conductivities for heat and electricity for the different metals, values are found which differ greatly[1] from those derived from the Peltier effect. Moreover, the experiments of Rubens and Hagen show that the electrical conductivity of metals for alternating currents of very high frequency remains practically the same as for steady forces, and the values of N which follow from these data are impossible[1] in view of the known values of the specific heat. Furthermore, Lees[2] measured the thermal and electrical conductivities of a number of metals down to the temperature of liquid air and found an increasing deviation from the law

$$\frac{\lambda}{\sigma} = \frac{4}{3}\frac{\alpha^2}{e^2}T.$$

A change in structure has a large effect on the thermal and electrical conductivities. For instance it has been found recently[3] that the resistance of mercury at 4.2° absolute drops suddenly from 0.11 to zero. Small impurities have large effects. Metals and alloys often behave in opposite ways. For example, the heat conductivity of the metals de-

[1] J. J. Thomson, Corpuscular Theory of Matter, pp. 76, 84.

[2] C. H. Lees, Phil. Tran., Royal Soc., Vol. 208, p. 381, 1908.

[3] H. Kamerlingh Onnes, Com. Phys. Lab. of Univ. of Leiden, No. 124, p. 23.

creases slightly with increasing temperature, while for the alloys it inincreases with the temperature. Moreover, the ratio $\lambda/\sigma T$ increases slightly between $-$ 180° C. and $+$ 20° C. for the metals, and decreases considerably for the alloys.

These facts cannot be explained by the present theories even when it is assumed, as Lorentz and Richardson[1] have done, that the distribution of the velocities of the electrons is that which corresponds to Maxwell's expression.

The strongest evidence against this conception of the electric current consists in the fact, shown by Nernst, that the specific heat of metals approaches zero as the temperature approaches the absolute zero. If the current were due to the motion of free electrons which are in temperature equilibrium with the metal, then the specific heat would be due mainly to the free electrons and would therefore, as in a gas, change very little with decreasing temperature. The question arises as to whether the electrons carrying the current take part in the specific heat.

Several modifications of the original theory have been proposed, but none of them gives an adequate quantitative explanation of all the phenomena. The various theories agree only in the fundamental assumption that the current is carried by electrons. This is in harmony with the general facts that the good conductors are metals, positive elements, ready to part with a negative electron; that the metals when struck by ultra-violet light or Roentgen rays, or when heated to a certain temperature, emit electrons; and that the current in the metals shows the Hall effect.

The decrease of the specific heat with decreasing temperature is at least qualitatively accounted for by Planck's theory of radiation. It is possible that the electrons have at low temperature no part in the specific heat of the metals, so that the specific heat is entirely due to the motion of the atoms or to their elementary oscillators. According to this conception there are no free electrons at all, at least at low temperatures, and the electrons escape only when they have acquired a sufficient amount of kinetic energy to overcome the attraction of the positive "rest-atom." Then there should be a definite relation between the energy of the electron and the energy of the atom.

We shall assume that the electrons part with the atom when their kinetic energy is proportional to the energy E of the atom. Moreover, for the energy of the atom, or the oscillator in the atom, we shall assume the expression given by Planck[2]

[1] Planck, Acht Vorlesungen über Theoretische Physik.

[2] O. W. Richardson, Trans. Am. Chem. Soc., Vol. XXI., 1912.

$$E = \frac{hn}{e^{\frac{hn}{kT}} - 1},$$

or, according to the modified theory,

$$E = \frac{hn}{e^{\frac{hn}{kT}} - 1} + \frac{hn}{2}.$$

Then the kinetic energy of the electron is given by

$$E_1 = \tfrac{1}{2}mv^2 = \gamma \frac{hn}{e^{\frac{hn}{kT}} - 1},$$

where γ is some constant, and from this equation we know v as a function of T. The constant term $hn/2$ has no effect in the present application of the Planck theory. If l is the mean free path and t the time during which the electron moves from one atom to the other, then

$$v = \frac{l}{t}.$$

The force acting on the electron in the field E' is $E'e$, and the acceleration

$$a = \frac{E'e}{m}.$$

The mean time during which this force acts is $t/2$ seconds and hence the field superposes a velocity

$$u = \frac{at}{2} = \frac{E'el}{2mv}.$$

The number of electrons passing through unit cross-section per unit time is

$$Nu = \frac{NE'el}{2mv},$$

and the current density

$$i = Nue = \frac{E'e^2Nlv}{2mv^2} = \sigma E'.$$

Whence

$$\sigma = \frac{e^2Nlv}{2mv^2} = \frac{Nlve^2}{4E_1} = \frac{Nlve^2.}{4\gamma \frac{hn}{e^{\frac{hn}{kT}} - 1}}. \qquad (1)$$

For the quantity of heat energy passing through unit area per unit time, we have

$$H = \frac{1}{3} Nvl \frac{\partial E_1}{\partial x} = \frac{1}{3} Nvl \frac{dE_1}{dT} \frac{dT}{dx} = \lambda \frac{dT}{dx}.$$

And

$$\lambda = \frac{1}{3} Nvl \frac{dE_1}{dT}. \tag{2}$$

Hence

$$\frac{\lambda}{\sigma} = \frac{4}{3e^2} \frac{dE_1}{dT} E_1. \tag{3}$$

Substituting in (3) the values of E_1 and dE_1/dT, we have

$$\frac{\lambda}{\sigma T} = \frac{4}{3} \frac{\gamma^2 h^3 n^3}{e^2 k} \frac{1}{T^3} \frac{e^{\frac{hn}{kT}}}{\left(e^{\frac{hn}{kT}} - 1\right)^3}. \tag{4}$$

If hn/kT is small, we can expand the exponential functions and equation (4) for the higher temperatures assumes the form

$$\frac{\lambda}{\sigma T} = \frac{4}{3} \gamma^2 \frac{k^2}{e^2} \left(1 - \frac{hn}{2kT}\right). \tag{5}$$

As T increases, according to equation (5), the values of $\lambda/\sigma T$ should approach a constant value and this agrees with the facts. Moreover, when the values of $\lambda/\sigma T$ are plotted against T in equation (4), the curve is found to be of the same form as the experimental curves which Lees obtained for the pure metals at low temperatures. Thus we have a formula which explains the behavior of $\lambda/\sigma T$ for pure metals and which also leads approximately to the right expression for the variation of the specific heat with the temperature. It agrees with Einstein's formula for specific heat; in fact, both formulæ rest upon Planck's expression for E.

It is not claimed that this theory is complete. It is merely suggested as a possible step in the right direction because it removes two important difficulties of the electron theory without introducing new contradictions. The phenomena of metallic conduction are so complicated that they cannot be explained by one simple group of assumptions. So far we have considered only the heat conductivity due to the electrons. The atoms themselves undoubtedly transfer a part of the heat motion as is shown by the fact that non-conductors of electricity have finite values of λ while σ is equal to zero. Moreover, there are good reasons for believing l, the mean free path, is a function of the temperature. This would follow from Richard's theory in regard to the variation of the radius of the atom. It should be pointed out that if we take the two most simple formulas

$$\lambda = \frac{1}{3} Nlv\alpha,$$

$$\sigma = \frac{Nle^2}{2mv},$$

and assume $\frac{1}{2}mv^2 = \alpha T$ and also $l = \text{const}/\sqrt{T}$, it follows that λ becomes independent of the temperature, while σ is inversely proportional to the absolute temperature. This agrees fairly well with experimental facts over a considerable range of temperature. That the mean free path has something to do with the conductivity is also shown by the Hall effect. H. Kamerlingh Onnes has found that the constant of the Hall effect for gold, silver and mercury, increases considerably near the temperature of liquid hydrogen.

Finally, the electric field may act on the atoms in a metal, tending to bring about a certain polarization which will have an effect on the conductivity for electricity and heat. If this were the case, we should expect the use of temperature baths to lead to a value of λ different from that obtained by electric heating.

It was the purpose of the present investigation to attempt to bring further evidence in favor of one of the different theories. The alkali metals were thought to be particularly suited to this purpose because they have properties quite different from those of the other metals. Alkali metals have a higher temperature coefficient of resistance than the other metals. The atomic heat and atomic volume are greater and the index of refraction smaller than for the ordinary metals. In their photoelectric properties they differ considerably from the other elements. All these properties indicate that the alkali metals are rich in electrons and that even the positive "rest-atoms" have considerable mobility.

So far as known, the heat conductivity of the alkali metals has hitherto not been measured. This is a constant of sufficient importance to make its determination worth while. Northrup[1] has determined the electrical conductivity of the alkali metals by a very good method and claims an accuracy of one half of one per cent. His results, however, do not agree well with those of former observers[2] and it was therefore considered important to check his work by an entirely different method.

II. Theory of the Method.

The original Kohlrausch[3] method, which was perfected by Jaeger and

[1] E. F. Northrup, Trans. Am. Electro-Chem. Soc., Vol. XX., 1911, p. 185.

[2] Mattheisen, Phil. Mag. (4), 12, 199, 1856; 13, 81, 1857. Bernini, Phys. Zeit., 5, 241, 1904.

[3] F. Kohlrausch, Gött. Nachr., S. 83, 1874; Pogg. Ann., 156, S. 616, 1875; Ann. der Phys., (4) I., 145, 1900.

Diesselhorst,[1] was used. It is both simple and reliable and it has the distinct advantage of giving the ratio of the heat and electrical conductivities directly. This method consists, briefly, in sending a steady electric current through a cylindrical rod of the metal to be investigated and measuring the temperature and potential difference at three equidistant points along the axis of the rod, while the temperatures of the ends of the rod and of the surrounding jacket are held constant. For the convenience of the reader the theory of the method, so far as it has any application to this investigation, will be given here in a simplified form.

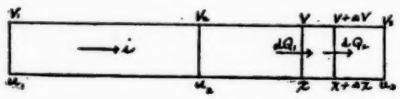

Fig. 1.

Referring to Fig. 1, let u and v represent the temperature and potential of any cross-section of the rod; and let

a = area of cross-section,

σ = electrical conductivity,

λ = thermal conductivity.

Let us assume that the Thomson effect is negligible and that λ and σ, for the small temperature interval considered, are constant. Then the current flowing through the rod is given by

$$i = \left(-\frac{dv}{dx}\right)\sigma a.$$

And the number of calories of heat developed in the elementary volume per unit time is

$$dQ = \frac{i^2}{\sigma} \cdot \frac{dx}{a} \cdot \frac{1}{J},$$

where J represents Joule's equivalent,

$$dQ = \left(\frac{dv}{dx}\right)^2 \sigma a \frac{dx}{J}.$$

The quantity of heat flowing into the elementary volume per unit time is

$$dQ_1 = \left(-\frac{du}{dx}\right)\lambda a,$$

and the quantity flowing out is, likewise, equal to

$$dQ_2 = -\frac{du}{dx}\lambda a - \frac{d^2u}{dx^2}\lambda a dx.$$

[1] Jaeger und Diesselhorst, Wiss. Abh. der Phys. Tech. Reich., 3, 269, 1890; Sitz. Ber. Der Berlin Ak. d.w., 38, 719, 1899.

For the stationary state

$$dQ + dQ_1 - dQ_2 = 0. \tag{1}$$

Substituting in this equation, we have

$$\left(\frac{dv}{dx}\right)^2 \frac{\sigma}{J} + \frac{d^2u}{dx^2}\lambda = 0. \tag{2}$$

Now the isothermal surfaces are also equipotential surfaces, if we assume that the temperature is constant for all points of the same cross-section, and the temperature depends upon the potential only. Then

$$\frac{du}{dx} = \frac{du}{dv}\frac{dv}{dx}.$$

And

$$\frac{d^2u}{dx^2} = \frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2 + \frac{du}{dv}\frac{d^2v}{dx^2}.$$

But

$$\frac{d^2v}{dx^2} = 0,$$

$$\frac{d^2u}{dx^2} = \frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2.$$

Substituting this value in equation (2), we have

$$\left(\frac{dv}{dx}\right)^2 \frac{\sigma}{J} + \lambda \frac{d^2u}{dv^2}\left(\frac{dv}{dx}\right)^2 = 0.$$

Or

$$\frac{d^2u}{dv^2} = -\frac{\sigma}{J\lambda}. \tag{3}$$

Integrating this equation, we have

$$\frac{\lambda J}{\sigma}u = -\frac{v^2}{2} + Av + B. \tag{4}$$

The integration constants, A and B, are readily evaluated by imposing the condition

$$u_1 = u_3 = u',$$

and the equation can be reduced to the form

$$\frac{\lambda}{\sigma} = \frac{1}{8}\cdot\frac{1}{J}\cdot\frac{(v_1 - v_3)^2}{u_2 - u'}, \tag{5}$$

where u_2 is the temperature of the middle of the rod, and u' is the temperature of either of the two sections equally distant from the middle.

Equation (5) would be true if no heat were lost through the lateral surface of the rod. This condition, however, cannot be realized experimentally and so it is necessary to apply a correction.

Let us change (5) slightly by expressing λ in watt-seconds, instead of calories, and put

$$V = \tfrac{1}{2}(v_1 - v_3),$$

$$U = u_2 - u' = u_2 - \tfrac{1}{2}(u_1 + u_3).$$

Then we have

$$\frac{\lambda}{\sigma} = \frac{V^2}{2U}. \tag{6}$$

In this equation, then, U stands for the value of the temperature difference, supposing that the surface of the rod were covered with a perfect heat insulator.

Now let Δ represent the observed value of the temperature interval $u_2 - \tfrac{1}{2}(u_1 + u_3)$; let u_0 represent the temperature of the surrounding jacket; and let

$$N = u_0 - u_2 + \tfrac{1}{6}\Delta.$$

Then, as Jaeger and Diesselhorst have shown,[1]

$$U = \Delta - \epsilon N, \tag{7}$$

where ϵ is a correction factor depending on the conductivity of the packing, the conductivity of the metal, and the dimensions of the rod experimented upon; and its value can be determined by experiment.

In the present work with the alkali metals, the values of λ/σ were computed by means of equations (6) and (7).

$$\epsilon = \frac{\Delta}{N},$$

for the case where no heating current is used. The method of obtaining this correction factor will be made clear in a later chapter.

III. APPARATUS.

End Baths.—The apparatus for controlling temperatures was constructed in the department shop. It was modeled after that of Jaeger and Diesselhorst, but certain modifications were necessary in order to protect the glass vacuum tubes which contained the alkali metals. The end baths were provided each with a flat brass lid and a rotary stirrer, as shown in Fig. 2, which was driven by a small motor. Fig. 3 indicates the method used to attach the glass tubes to the end baths. In a way

[1] Wiss. Abh. der Phys. Tech. Reich., 3, 285, 1900.

to be described in detail later, the metal to be studied was poured into glass tubes one or two centimeters in diameter and 30 cm. long. The ends of the tube were closed by copper discs, 2 mm. thick and 5½ cm. in diameter. By means of suitable brass rings, each provided with six

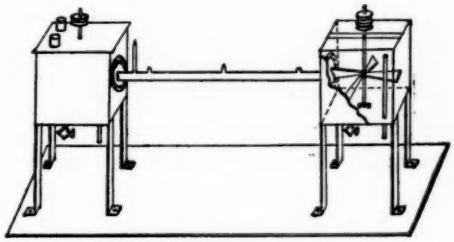

Fig. 2.

screws, the end-discs were attached to annular diaphragms which, in turn, were mounted against the end baths in a similar way so that the alkali metal and the water were separated only by the thin discs of copper. The soft-rubber diaphragms served as a protection for the glass tubes against mechanical strains.

The heating-current terminals were introduced beneath the heads of three of the screws symmetrically placed with respect to the center of the discs.

Brass Jacket.—The temperature of the atmosphere of the tubes was controlled by pumping water from a reservoir through a cylindrical

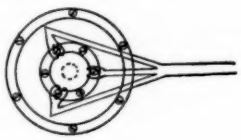

Fig. 3.

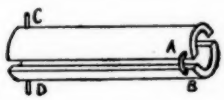

Fig. 4.

brass jacket by means of a small turbine. This jacket was made in two independent parts which were connected at A and B (Fig. 4), and similarly on the opposite side, by short rubber tubes, thus making it necessary for the water to flow the entire length of both semi-cylinders before leaving the jacket. The wires of the thermo-couples were introduced between the two parts of the jacket and were insulated from the brass by thin strips of mica.

The temperature, u_0, of the jacket was measured by two Beckmann thermometers, mounted deep within vertical glass tubes through which the water flowed, so that no stem corrections were necessary. More-

over, these thermometers were placed so that their bulbs were at exactly equal distances from the points C and D respectively. The tubes leading from the jacket to the thermometers were made as short as possible and were packed each with the same number of layers of asbestos paper. Likewise, the glass tubes containing the thermometers were packed similarly so that, even though the two indicated temperatures which differed considerably when working far from room-temperature, still the arithmetic mean of the two readings gave the true mean temperature of the water in the jacket.

The space surrounding the tube within the brass jacket was packed tight with cotton wool and the outside surface of the jacket was wrapped with fourteen layers of heavy cotton flannel.

Galvanometer.—The galvanometer used was of the D'Arsonval type and designed especially for work with thermo-couples. It has a resistance of 230 ohms, a period of four seconds, and a sensibility of 210 megohms for a scale distance of 1 meter. By means of an unusually good lens, however, the image of a lamp filament was brought to a sharp focus on a scale 5½ meters distant from the mirror. At 5½ meters the sensibility was 8.6×10^{-10} amperes per millimeter deflection. The E.M.F. of the copper-constantan thermo-couples was about 40 microvolts per degree, giving deflection of 0.2 mm. per 1/1000 degree. Thus a change in temperature of one thousandth of a degree could be detected.

Ammeters and other Apparatus.—Except for the potassium tube, where the value of the heating current sometimes exceeded 150 amperes, a new Siemens and Halske ammeter was used. It was standardized by means of a Wolff potentiometer, Weston standard cell, and a standard 0.01 ohm resistance. For the data on potassium a Weston direct reading ammeter (0–200) was used. This was put in series with the new ammeter, mentioned above, and calibrated for the range over which it was used.

All of the standard thermometers except No. 17,481 were standardized at the Reichsanstalt. No. 17,481 was certified by the Bureau of Standards. These thermometers were graduated to tenths of a degree.

An Otto Wolff potentiometer, Otto Wolff resistance boxes, and a Weston standard cell were used.

The heating current was supplied by the department storage battery.

Arrangement of the Electrical Apparatus.—The potentiometer, P, was connected as shown in Fig. 5. B_1 was a small storage cell; B_2, the standard cell; R_1, R_2 and R_3 were resistance boxes. By adjusting R_3 at the beginning of a run, the potential difference from A to C was made equal to the E.M.F. of the standard cell. R_1 and R_2 were kept constant.

The switches and keys of the potentiometer circuit which had to be

operated continually while taking readings, were grouped together on one switchboard shown diagrammatically in Fig. 6. C_1 and C_2 represent

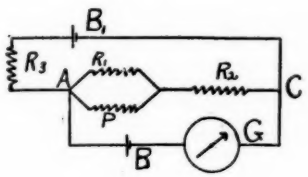

Fig. 5.

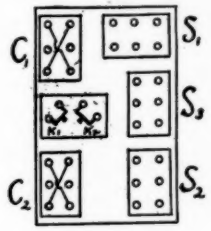

Fig. 6.

commutators of the rocker type; S_1, S_2 and S_3 were two-way switches of the rocker type; K_2 and K_3 were ordinary mercury keys. Six blocks of paraffine were mounted upon a glass plate, 30 × 40 cm., in the positions indicated. The thirty-two mercury wells which were sunk in the paraffine, were all lined by small glass cups which served as supports for the metal rockers. These rockers were all made of copper and only copper wires dipped into the mercury cups, all being wound from the same spool. In this way, contact potential differences were reduced to a minimum.

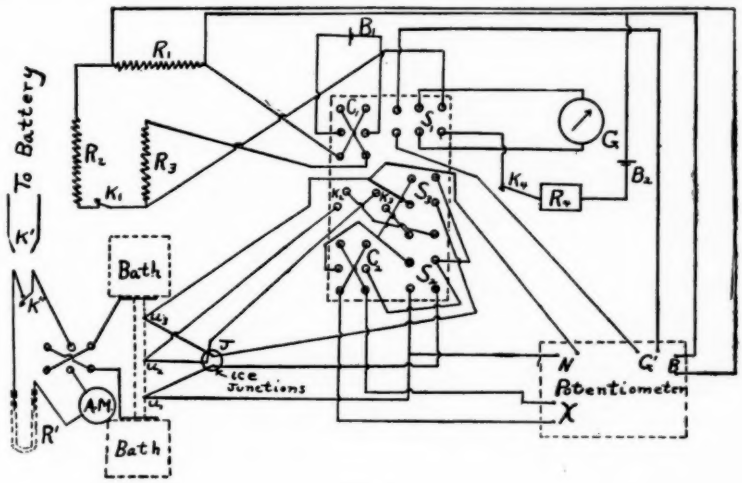

Fig. 7.

Fig. 7 shows a diagram of the exact connections of the electric circuits and the relative positions of the apparatus, with the exception of the galvanometer which was on a wall bench on the opposite side of the room, 5½ meters away. The ammeter, A.M., commutator C', controlling

resistance R', and key K'', were all within easy reach of the observer. K'' was a short-circuiting key to avoid arcing when the rocker of C' was thrown over. R_4 was simply a protective resistance for the galvanometer and standard cell, and could be cut out of the circuit by a suitable plug.

IV. EXPERIMENTAL DETAILS.

Construction of Thermo-couples.—Since the alkali metals dissolve ordinary solder, it could not be used for the junctions which were placed in the tubes. Moreover, it was not an easy matter to hard-solder the junctions without burning the minute copper wires. Several attempts to do this having failed, it was decided to try the use of mechanical contacts. The fine copper wire, 0.12 mm. in diameter, was wound around the constantan wire (diam. 0.18 mm.) for a distance of about 2 mm. The shape of these junctions was admirably adapted to the double purpose of measuring both the temperature and potential difference between two cross-sections. They were mounted in a tube of sodium-potassium alloy but the data was inconsistent and on removing the junctions from the tube and attempting to check their calibration, it was found that two of the three calibration curves had shifted by an amount equivalent to more than one tenth of a degree.

So it was considered necessary to solder the wires together. The method which finally succeeded was as follows. Nearly equal weights of copper and silver were melted together with a small blast flame. A junction formed by two or three turns of the copper wire around the constantan, was moistened and covered with powdered borax. Then, at a time when the temperature of the silver-copper alloy was just above the melting point, the junction was dipped beneath the surface of the globule and quickly removed.

Junctions could be soldered in this way without any injury to the delicate wires. Such junctions, therefore, were used in the last three tubes experimented upon,—the three for which the data are given in this paper. The ice junctions were soldered with ordinary soft-solder.

For the alloy tube and the potassium tube, copper wire 0.12 mm. in diameter was used. However, it was found to be almost impossible to go through the long process of calibrating the thermo-couples, mounting them into the tube, filling the tube, and finally mounting the tube between the water-baths, without breaking one of these frail wires at some point where it could not be soldered,—thus involving the loss of the thermo-couple and several days' work. Consequently, somewhat larger copper wires were used in the sodium tube. In this case the diameter of the wire was 0.16 mm. It can be shown, however, that the error due

to the conductivity of this wire was negligible for the conditions under which it was used. For all three of the tubes the constantan wire used had a diameter of 0.18 mm.

Platinum-constantan thermo-couples were used in the lead rod because, at that time, it was thought platinum wire would be used in the case of the alkali metals since it could be sealed into the glass, but the plan proved impracticable.

Calibration of the Thermo-couples.—The thermo-junctions and thermometer were mounted within a large Dewar flask which contained also a rotary stirrer. For the lower temperatures salt and ice were used to keep the temperature from rising, while for the higher temperatures steam was introduced slowly through a small tube near the wall of the flask at a point diametrically opposite the position of the thermo-junctions and thermometer. The temperature in this way could be held very steady by regulating the gas pressure of the three Bunsen flames which heated the boiler. The rotary stirrer was run by a small motor.

For the first few calibration curves a cathetometer was used to read the thermometer scale. This, of course, was a most accurate method, but it involved the difficulty of holding the temperatures constant for several minutes at a time, since the vernier had to be adjusted and read both before and after balancing the potentiometer for direct and reversed currents. Consequently, it was decided to try a direct-reading eye-piece attached to the stem of the thermometer. By this method the data for a point on the calibration curve could be obtained so much more quickly that the loss in accuracy of the scale reading was almost compensated by the gain in time and consequent smaller variation in the temperature. Readings were taken at intervals of about one or two tenths of a degree over the particular range where the curves were to be used and, when the points were plotted, there was no doubt about the proper position of the line.

The curves obtained in this way were reliable to about three or four thousandths of a degree, for the measurement of temperature differences; and, since this was as high a degree of accuracy as was required in the calibration, the use of the cathetometer was abandoned in favor of the quicker and less laborious procedure.

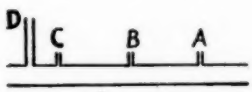

Fig. 8.

Preparation of the Tubes.—The kind of tube used to contain the alkali metals is shown in Fig. 8. The side tubes *A*, *B* and *C*, through which the thermo-junctions were introduced, were about 2 mm. in diameter and 10 cm. apart. They were sealed on in such a way as to change the

cross section of the main tube as little as possible. The filling tube *D* was always placed at least 4 cm. from *C*. The diameters of the tubes are given in the data tables. The entire length in each case was about 30 cm.

Considerable difficulty was met in devising a method of sealing in the thermo-junctions so that a vacuum could be maintained at temperatures above the melting point of sealing wax. It was finally accomplished in the following way. The two wires of the junctions, one of which in each case was contained in a minute, slightly funnel-shaped glass tube for insulation purposes, were first sealed into the tube by means of "Quixo Caementium." This is a mineral cement, a commercial article, which was purchased from one of the local dealers. It dries very hard but it is somewhat porous and will hold a vacuum only a short time. Consequently, after the caementium had dried it was covered over with a layer of sealing wax. A kind called De Khotinsky cement was used because it has a higher melting point than the red, "Bank of England" wax. The caementium held the thermo-junctions rigidly in their positions and when the tube was heated the air pressure could not force the soft wax into the tube.

After grinding the ends of the tube they were fitted into circular grooves in the copper end-disks, about 1.5 mm. deep. These joints were filled with litharge (PbO) mixed in boiled linseed oil, and baked for several hours at a temperature of about 100° C. When thoroughly dry and solid they were covered with a thick layer of the Khotinsky sealing wax. The reason for using litharge in place of caementium, for sealing on the end discs, was the fact that it does not dissolve in water,—thus reducing the fire-risk in case of accident.

Before the end discs were sealed on, an accurate scale was introduced within the tube and the thermo-junctions bent into positions which spaced them exactly 10 cm. apart. They extended about 3 mm. into the tube.

The sodium and potassium tubes were prepared as described above. Sealing wax alone, however, was used in the case of the sodium-potassium alloy and for this reason no data could be taken with this tube for temperatures above 45°.

Filling the Tubes.—The method of filling the tubes is illustrated in Fig. 9. The sodium or potassium was introduced into the bulb *D* through an opening at *G*. The tube was then sealed at *G* and the Gaede pump started. After melting the metal, it was kept hot for an hour or more during the exhaustion, in order to drive off all traces of the oil. When the crust finally appeared dry and black, and the discharge tube *F* showed only the presence of the alkali vapor, the system was sealed off at *E*.

Then, holding *AB* in a horizontal position and keeping it hot with Bunsen flames, the tube *D* was tilted and the bright, pure metal poured through a system of small funnels at *C* which held back all of the dross.

It was a very difficult matter to fill a tube because of the formation of bubbles due to vapor pressure, and further, because of the contraction of the metal on cooling. The only way it could be done at all was to pour in metal a little at a time and allow it to solidify before adding any more. Thus it was necessary to melt the successive portions together to avoid layers and this local heating often involved the loss of a tube, either by breaking the glass or by letting the air in through the softened cement at one of the thermo-junctions. When filled, the tube *AB* was sealed off at a stricture *H* and it was then ready to be mounted between the water-baths.

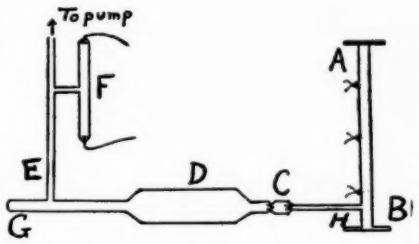

Fig. 9.

Purity of the Metals.—The sodium and potassium were purchased from Eimer and Amend and, in a personal letter from the company, were claimed to be "very pure." I am indebted to Dr. G. McP. Smith, of the chemistry department, for the following test on the purity of these metals.

Sodium.

1. Free from iron (KCNS test).
2. Free from calcium ($(NH_4)_2C_2O_4$ test).
3. Free from magnesium (Na_2HPO_4 test).
4. Free from aluminum (no ppt. with NH_4OH–Na_2HPO_4 test).
5. Free from potassium (H_2PtCl_6 test).

Spectroscopic test also negative, but conditions were not most favorable at time of test.

Potassium.

1. Free from iron.
2. Free from calcium.
3. Free from magnesium.
4. Free from aluminum.
5. Contains enough sodium to give a test with the spectroscope. Undoubtedly only a trace.

Method of Control of Temperatures.—The apparatus for controlling temperatures has been described in Chapter III. For the determinations above room temperature, the temperatures were adjusted and held constant by means of Bunsen flames, one under each end-bath and three beneath the large reservoir from which the water was pumped through the brass jacket. For the lower temperatures the turbine was discarded and cold water was run through the jacket by gravity pressure, the rate

of flow being regulated by a small globe valve. In these determinations the temperatures of the end baths were watched constantly by a student helper and were maintained by the continuous addition of snow and salt.

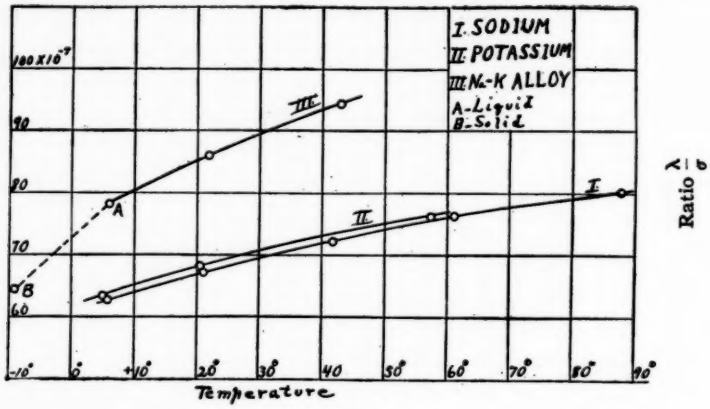

Fig. 10.

Regulation of the Heating Current.—As already mentioned, the currents from the large storage battery were remarkably constant. The slight regulation necessary was accomplished with a mercury rheostat. The U-tube, which was made of glass tubing 2.6 cm. in diameter, stood 80 cm. high. Continuous adjustments could be made by varying the position of the copper-plated iron rods which dipped into the mercury.

V. Data Tables and Curves.

In order to cut down the length of the paper the original data will be given only for a few typical runs. They will serve to illustrate the method

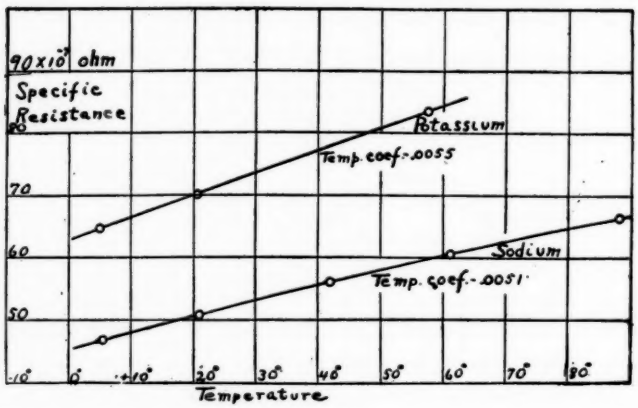

Fig. 11.

of taking observations and to indicate the degree of consistency obtained at different temperatures. In the tables which follow these "specimen runs," merely the final results are recorded.

Meaning of Symbols.—In all the data tables the following notation is used:

r_1, r_3 = balance-resistance on potentiometer dial for thermo-couples No. 1 and No. 3.

r_2 = balance-resistance for thermo-couple No. 2 at middle of tube (or rod).

r' = balance-resistance when reading P.D.

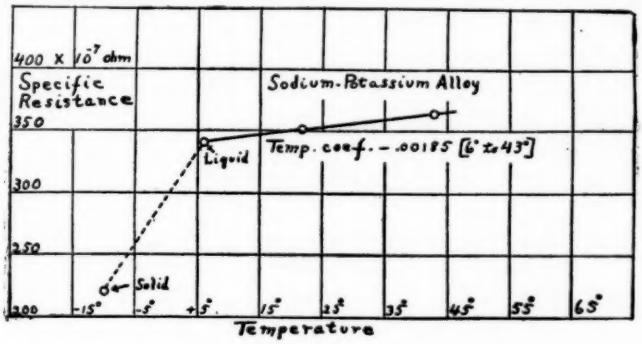

Fig. 12.

u_1, u_2, u_3 = temperatures corresponding to resistances r_1, r_2, r_3.

u_0 = temperature of the brass jacket.

$u' = \frac{1}{2}(u_1 + u_3)$.

$t_m = \frac{1}{2}(u' + u_2)$ = temperature for which the values of σ/λ, ρ and λ are taken in plotting curves.

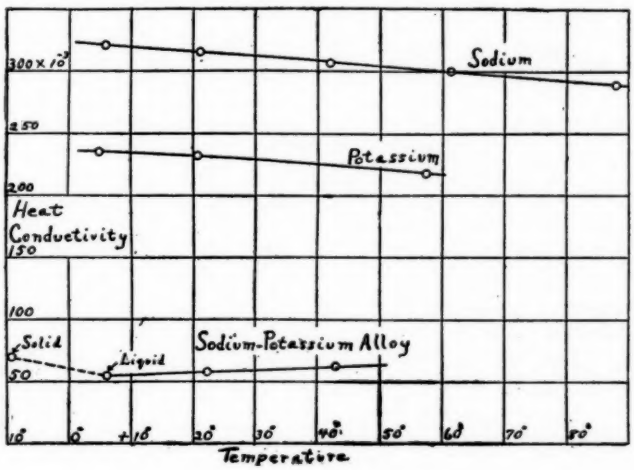

Fig. 13.

V = one half of the P.D. between the two points which were held at the same temperature.

I = value of heating current in amperes.

$\Delta = u_2 - u'$. $\quad U = \Delta - \epsilon N$.

$N = u_0 - u_2 + \frac{1}{6}\Delta$. $\quad \epsilon = \Delta/N$ when $I = 0$.

The letters D and R in the tables represent direct and reversed currents through the potentiometer to eliminate contact potential differences.

No. 2606 and No. 2607 refer to the two Beckmann thermometers which gave the temperature of the brass jacket.

TABLE I.

Constants for the Three Tubes.

Substance.	Inside Diameter.	Area a.	Effective Length l.
Na-K Alloy.....	1.562 cm.	1.916	20 cm.
Potassium.....	1.620 cm.	2.061	20 cm.
Sodium.....	1.234 cm.	1.196	20 cm.

$$\rho = \frac{Ra}{l} = .0958R = \frac{.0958 \times 2V}{I}, \text{ for sodium-potassium alloy.}$$

$$\rho = \frac{0.103 \times 2V}{I}, \text{ for potassium tube.}$$

$$\rho = \frac{.0598 \times 2V}{I}, \text{ for sodium tube.}$$

TABLE II.

Correction Factor for Potassium Tube (Specimen Run).

	r_1	r_3	r_2	u_0 No. 211.	u_0 No. 212.
D	187.8	187.7	197.2	2.20	1.36
R	186.8	186.8	196.2		
D	187.5	187.8	197.0	2.18	1.35
R	186.6	186.9	196.2		
D	187.5	187.8	197.0	2.19	1.30
R	186.7	186.9	196.3		
D	187.5	187.6	196.9	2.20	1.27
R	186.7	186.7	196.2		
D	187.1	187.8	196.9	2.23	1.24
R	186.4	186.9	196.1		

Left bath held at 18.4°; right bath at 18.3°.

Mean temperature on No. 211 = 2.20 + 33.06 = 35.26°.

Mean temperature on No. 212 = 1.30 + 32.91 = 34.21°.

$u_0 = \frac{1}{2}(35.26 + 34.21) = 34.74°$ C.

Mean $r_1 = 187.1$ ohms; $u_1 = 20.025°$.

Mean $r_3 = 187.3$ ohms; $u_3 = 19.965°$.

Mean $r_2 = 196.6$ ohms; $u_2 = 20.925°$.

$\Delta = 20.925 - 19.955 = 0.930°$.

$N = 34.74 - 20.925 + 0.155 = 13.97°$.

$$\epsilon = \frac{\Delta}{N} = \frac{0.930}{13.97} = .066.$$

TABLE III.

Sodium-Potassium Alloy at 5.7° (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r'	r_1	r_3	r_2	u_0 No. 2606.	u_0 No. 2607.	r_1	r_3	r_2	r'
D	3667	33.9	35.9	68.4	4.05	4.30	34.9	35.7	68.8	3661
R		35.2	37.3	69.8	4.10	4.25	36.2	37.2	70.2	
D	3656	34.2	35.9	68.5	3.95	4.15	34.9	35.6	68.4	3664
R		36.0	37.3	69.9	3.95	4.20	36.7	37.2	70.3	
D	3656	34.2	35.9	68.6	3.94	4.20	34.8	35.5	68.4	3661
R		36.0	37.4	70.0	3.90	4.15	36.8	37.2	70.4	
D	3657	34.2	35.9	68.4	3.95	4.15	34.6	35.4	68.2	3663
R		36.1	37.6	70.2	3.93	4.15	36.6	37.2	70.2	
D	3658	34.1	35.7	68.3	3.98	4.17	34.6	35.4	68.1	3662
R		35.9	37.6	70.1	3.93	4.15	36.6	37.2	70.1	

Left bath at $-0.4°$; right bath at $0°$.
6 volts, 6 sets in parallel. $I = 41.2$ amp.
Mean $r_1 = 35.4$ ohms; $u_1 = 4.02°$. Mean reading on No. 2606 = 3.97.
Mean $r_3 = 36.6$ ohms; $u_3 = 4.04°$. Mean reading on No. 2607 = 4.20.
Mean $r_2 = 69.3$ ohms; $u_2 = 7.42°$.
Mean temp. on No. 2606 = 3.97 + 2.41 = 6.38° C.
Mean temp. on No. 2607 = 4.20 + 2.76 = 6.96° C. } $u_0 = 6.67°$ C.
Mean $r' = 3{,}660$ ohms. $2V = 3660 \times 4 \times 10^{-6} = .01464$ volt.

Sample Calculation.

$$\Delta = 7.42 - 4.03 = 3.39. \quad t_m = \tfrac{1}{2}(4.03 + 7.42) = 5.7°.$$
$$N = u_0 - u_2 + \tfrac{1}{6}\Delta = 6.67 - 7.42 + 0.57 = -0.18.$$
$$U = \Delta - \epsilon N = 3.39 + 0.22 \times 0.18 = 3.43.$$
$$\frac{\sigma}{\lambda} = \frac{.2U}{V^2} = \frac{6.86}{(.00732)^2} = 128.1 \times 10^3.$$
$$\rho = \frac{.0958 \times .01464}{41.2} = 34040 \times 10^{-9} \text{ ohm}.$$
$$\lambda = \frac{10^5}{4.19 \times 128.1 \times 3404} = .0547 \text{ cal}.$$

TABLE IV.

Sodium at Room Temperature (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r_1	r_3	r_2	r'	u_0 No. 2606.	u_0 No. 2607.	r_1	r_3	r_2	r'
D	187.6	190.9	218.0	3096	5.40	5.48	187.6	188.9	217.1	3099
R	187.0	190.3	217.4				188.7	188.0	217.9	
D	188.3	190.5	218.0	3093	5.43	5.52	187.7	188.9	217.3	3098
R	187.3	189.6	217.2				189.5	187.9	218.2	
D	188.7	190.9	218.6	3093	5.48	5.56	188.2	189.0	217.6	3098
R	187.7	190.3	217.6				189.3	188.2	218.4	
D	188.2	190.9	218.5	3093	5.53	5.61	188.1	188.9	217.4	3098
R	187.4	190.2	217.5				189.4	188.1	218.2	

12 volts, 12 sets in parallel. $I = 146.3$ amp.
Left bath held at 14.8°; right bath held at 15.9°.

Mean $r_1 = 188.2$; $u_1 = 20.08°$. Temp. on No. 2606 = 5.46 + 18.08 = 23.54.
Mean $r_3 = 189.5$; $u_3 = 20.12°$. Temp. on No. 2607 = 5.54 + 18.05 = 23.59.
Mean $r_2 = 217.8$; $u_2 = 23.01$. $u_0 = 23.57°$ C.
Mean $r' = 3{,}096$ ohms. $2V = 3{,}096 \times 4 \times 10^{-6} = .01238$ volt.
$\Delta = 2.91$. $N = 1.05$. $U = 2.85°$. $t_m = 21.5°$.

TABLE V.

Potassium at 57.8° (Specimen Run).

	Main Current Direct.					Main Current Reversed.				
	r'	r_1	r_3	r_2	u_0 No. 2606.	u_0 No. 2607.	r_1	r_3	r_2	r'
D	3075	560.6	554.4	584.5	3.38	2.75	557.6	558.4	584.4	3070
R		559.0	556.2	582.6	3.37	2.76	556.0	559.8	583.0	
D	3071	556.0	553.5	582.8	3.38	2.76	555.7	557.9	583.6	3070
R		557.8	555.2	581.0	3.42	2.77	553.8	559.6	582.0	
D	3078	557.4	554.9	584.1	3.43	2.78	557.7	557.6	584.3	3069
R		558.9	556.7	582.3	3.48	2.81	555.4	559.7	582.4	
D	3078	553.6	555.9	584.3	3.42	2.83	558.1	555.3	584.3	3079
R		555.3	560.6	582.5	3.35	2.81	555.6	557.1	582.4	
D	3074	554.4	555.9	584.4	3.27	2.73	557.8	555.2	584.0	3074
R		556.2	558.6	582.6	3.25	2.70	555.4	557.0	582.2	

16 volts, 8 sets in parallel. $I = 148.1 \times 1.026 = 152.0$ amp.
Left bath at 51.0°. Right bath at 51.3°.
Mean $r_1 = 556.6$; $u_1 = 56.625°$. Temp. on No. 2606 = 3.38 + 54.98 = 58.36.
Mean $r_3 = 557.4$; $u_3 = 56.630°$. Temp. on No. 2607 = 2.77 + 55.13 = 57.90.
Mean $r_2 = 583.2$; $u_2 = 59.070°$. $u_0 = 58.13°$.
Mean $r' = 3074$ ohms. $2V = .012296$ volt.
$\Delta = 2.443°$. $N = -0.53$. $U = 2.478°$. $t_m = 57.8°$.

TABLE VI.

Values of Correction Factor ϵ.

Substance.	u_0	u_2	Δ	N	ϵ
Lead rod	21.7	16. 7	0.918	5.38	0.171
Na-K alloy	21.19	15.40	1.35	6.01	0.224
	24.46	19.86	1.02	4.77	0.214
Potassium	34.74	20.925	0.930	13.970	0.066
Sodium	41.80	18.66	1.38	23.37	0.059

TABLE VII.

Complete Results for Lead (Commercially Pure).

Run No.	u_0	u_2	t_m	$2V$ $10^{-5}\times$	Δ	N	U	I Amp.	σ/λ $10^{8}\times$
1	21.64	21.94	20.6	1253	2.671	0.14	2.647	51.0	134.6
2	21.65	23.60	21.7	1566	3.838	−1.32	4.062	63.3	132.5
3	21.71	23.28	21.3	1588	4.046	−0.90	4.199	64.3	133.2

Remark.—For run No. 3, the lead rod was inside of a close-fitting glass tube.

TABLE VIII.

Complete Results for Sodium-Potassium Alloy.
(Masses taken proportional to the atomic weights.)

Run No.	u_0	u_2	t_m	$2V$ $10^{-5}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	−8.30	−8.28	−10.6	1511	4.56	+0.74	4.40	66.0	154.4	2193	.0705
2	−9.40	−6.37	− 8.9	1682	5.00	−2.20	5.48	72.9	155.2	2210	.0696
3	+6.67	7.42	5.8	1464	3.39	−0.18	3.43	41.2	128.1	3404	.0547
4	6.66	8.07	6.2	1588	3.83	−0.77	4.00	44.6	127.0	3411	.0551
5	22.40	23.936	22.0	1684	3.931	−0.88	4.122	45.9	116.3	3515	.0584
6	22.54	24.075	22.1	1702	4.003	−0.86	4.190	46.2	115.9	3527	.0584
7	22.66	22.395	20.7	1500	3.453	+0.84	3.271	40.9	116.2	3513	.0585
8	43.90	44.54	42.9	1550	3.17	−0.11	3.19	40.8	106.1	3640	.0619

TABLE IX.

Complete Results for Potassium.

Run No.	u_0	u_2	t_m	$2V$ $10^{-5}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	5.91	5.790	5.0	881	1.557	+0.38	1.531	141.9	158.2	649.2	0.232
2	6.58	5.810	5.0	862	1.525	+1.02	1.454	137.9	156.5	644.2	0.237
3	21.16	21.670	20.7	1035	1.965	−0.18	1.978	151.6	147.7	703.5	0.230
4	21.22	21.590	20.6	1030	1.920	−0.05	1.923	151.2	145.1	701.5	0.234
5	21.45	21.675	20.9	932	1.603	+0.04	1.600	137.6	147.4	698.0	0.232
6	58.13	59.070	57.8	1230	2.443	−0.53	2.478	152.0	131.1	833.8	0.218
7	57.91	58.510	57.4	1184	2.312	−0.21	2.326	147.3	132.4	835.3	0.216

TABLE X.

Complete Results for Sodium.

Run No.	u_0	u_2	t_m	$2V$ $10^{-5}\times$	Δ	N	U	I Amp.	σ/λ $10^3\times$	ρ Ohm $10^{-8}\times$	λ Cal.
1	7.20	6.97	5.7	1152	2.68	+0.68	2.64	147.7	159.0	466.4	0.321
2	7.75	7.22	5.8	1176	2.82	+1.00	2.76	150.7	159.5	466.7	0.321
3	23.42	22.12	20.9	1110	2.385	+1.70	2.283	130.6	148.2	508.3	0.317
4	23.57	23.01	21.5	1238	2.91	+1.05	2 85	146.3	148.8	506.0	0.317
5	43.32	43.44	42.1	1207	2.57	+0.31	2.55	128.3	139.7	562.6	0.304
6	44.97	43.38	41.7	1360	3.32	+2.14	3.19	145.5	138.1	559.0	0.309
7	62.30	62.84	61.3	1390	3.15	+0.01	3.15	137.2	130.4	605.8	0.302
8	63.11	62.83	61.4	1320	2.93	+0.77	2.88	130.7	132.1	604.0	0.299
9	89.01	89.43	88.1	1309	2.67	+0.03	2.67	118.0	124.8	663.4	0.288

VI. DISCUSSION OF RESULTS.

In using the experimental method of obtaining the value of the correction factor ϵ for the alkali metals, it was necessary to assume that for the steady state the temperatures at corresponding points on the inside and outside surfaces of the glass tube were equal; *i. e.*, that the tempera-

ture gradient through the walls of the glass tube could be neglected in comparison with the drop in temperature through the cotton wool. One reason for making the runs with the lead rod was to find out if this assumption would introduce an error large enough to be detected. Table VII. answers the question. The fact that the value of σ/λ for run No. 3 falls between those for runs No. 1 and No. 2, proves that the effect of surrounding the rod with the glass was smaller than other experimental errors. Lead was chosen for this experiment because of its low heat conductivity. The glass wall would have a still smaller effect in case of the sodium and potassium.

Another reason for taking the data for lead was to have a means of comparing my results with those of Jaeger and Diesselhorst. In this connection it should be noted that my average value of σ/λ for lead at 21.5° is 133.4×10^3 while that of Jaeger and Diesselhorst for pure lead, when reduced to 21.5°, is 138.2×10^3. This was considered a good check because the lead I used was only commercially pure. The presence of impurities always reduces the value of σ/λ.

As to accuracy of results it should be pointed out that for each run steady conditions were held for one to two hours and readings were taken continually during this time. Thus each value of u_1, u_2 and u_3, used in the calculations, depends upon sixteen to twenty readings on the potentiometer, while the values of V are computed from the mean of eight to ten readings. The current could be maintained much more nearly constant than could the temperatures and therefore the potential difference did not need to be read so often. Moreover, with one or two exceptions, every point on the curves represents the mean result of two or three independent runs.

The curves for λ/σ bend more than was expected. It would be interesting to know whether they become straight lines at higher temperatures. Judging from the behavior of other metals, this should be expected. Moreover, when $\lambda/\sigma T$ is plotted against T, these curves slope downward slightly with increasing temperature while Lees's curves for most of the pure metals bend slightly upward at ordinary temperatures. Thus sodium and potassium, like nickel, are irregular in this respect. It should be noted that the heat conductivities of sodium and potassium decrease slightly with increasing temperature, while the heat conductivity of the alloy *increases* with the temperature. This is the law followed by most metals and their alloys. The temperature coefficients of sodium and potassium are extremely high.

The mean values of the specific resistance of sodium and potassium at room temperature and the temperature coefficients are given below for convenience of comparison.

spec. res. of Na at 21.7° C. = 5072 × 10^{-9} ohm/cm.³.
spec. res. of K at 20.7° C. = 7010 × 10^{-9}
temp. coef. of Na = .00513, range 6° to 88°
temp. coef. of K = .00552, range 5° to 58°

Northrup's Results.

spec. res. of Na at 20° C. = 4873 × 10^{-9}
spec. res. of K at 20° C. = 7116 × 10^{-9}
temp. coef. of Na = .0053, range 20° to 80°
temp. coef. of K = .0058, range 20° to 50°

Matthiesen's Result.

spec. res. of Na at 21.7° C. = 4464 × 10^{-9}

Bernini's Results.

spec. res. of Na at 0.0° = 4739 × 10^{-9}
spec. res. of K at 0.0° = 6644 × 10^{-9}

Bernini's results, when reduced to room temperature, are found to be higher than mine and Northrup's, while Matthiessen's value is seen to be lower. It is thought that my results agree with Northrup's as closely as could be expected, considering the wide difference in method. Indeed his method is the more accurate one for electrical conductivity. Consequently, the results of this investigation may be said to confirm Northrup's work on the resistance of sodium and potassium. The slightly smaller values of the temperature coefficients suggest that the metals used in this work may not have been quite as pure as those Northrup used.

Summary.

1. The electrical conductivities of sodium, potassium and sodium-potassium alloy have been measured and the results are in agreement with the values obtained by Northrup.

2. The heat conductivities of the alkali metals have been measured for the first time, as far as known.

3. The temperature coefficients of these conductivities have been determined.

4. The resistance-temperature coefficients of potassium and sodium are extremely high.

5. The values of the ratio σ/λ for the alkali metals are extremely high.

6. The alkali metals behave in no exceptional way as regards the absolute values of the thermal and electrical conductivities at ordinary temperatures.

7. As a check on the method, the ratio σ/λ was determined for lead at room temperature and the value agrees with the one obtained by Jaeger and Diesselhorst.

8. A modification of the electron theory of metallic conduction has

been suggested which accounts for the variation of the specific heat with the temperature, and also explains the curves which Lees obtained for the ratio $\lambda/\sigma T$ for the pure metals at low temperatures.

In conclusion, I wish to acknowledge my indebtedness to Professor A. P. Carman, who has followed this work with continued interest, placing at my disposal all the facilities necessary for the investigation; and to Professor Jakob Kunz, under whose direction the work was done, for many good suggestions and for invaluable assistance in filling the tubes. I also wish to thank Dr. G. McP. Smith, of the chemistry department, who analyzed the metals used in this investigation.

LABORATORY OF PHYSICS,
UNIVERSITY OF ILLINOIS,
May, 1913.

Note.—Since this paper was written, I note in the April number of Science Abstracts, which has just come, that W. Wien has published an article on "Electric Conduction in Metals" based upon the "quanta hypothesis." His theory may be similar to the modification suggested in this paper. The article referred to is not accessible in our library.

J. W. H.

COMPARATIVE STUDIES OF MAGNETIC PHENOMENA. V.

Change in Electrical Resistance Due to the Orientation of Oblate Spheroids within the Conductor.[1]

By S. R. Williams.

Introductory.

THE change in electrical conductivity of ferromagnetic metals when subjected to a magnetic field was first observed in iron and nickel by Lord Kelvin[2] in 1856. His results showed that in both metals the electrical resistance was increased in a direction parallel to the magnetic lines of force and decreased in a direction normal. The qualitative results obtained by Lord Kelvin were for the most part confirmed by Adams,[3] deLucchi,[4] Beetz,[5] Tomlinson[6] and Goldhammer.[7] Beetz, in working with iron wires, failed to find any change in resistance in transverse fields. Tomlinson carried out some very extensive studies on the physical properties of certain metals and among them the alteration of electrical conductivity due to magnetic fields. His results are summed up in the following: "The electrical resistance of annealed iron and annealed steel, very hard steel, nickel, cobalt, bismuth and zinc are all increased by longitudinal magnetization." For transverse magnetization experiments were carried out in which the wires were circularly magnetized and a decrease in resistance was found. Goldhammer, from considerations of the Hall effect, was led to believe that there must be a change in resistance in all substances and greatest in those showing the largest Hall effect, as for instance in Te, Bi, Sb, Ni, Fe and Co. He did find a change in resistance in all of these but in Ag, Au and brass the effect was not large enough to measure with certainty. At the time of Lord Kelvin's experiments many expressed the view that the change in resistance was due to the mechanical deformations of the substances used. Goldhammer raised objections to this viewpoint and to obviate any

[1] Presented at the Cleveland meeting of the Physical Society, Dec. 30.

[2] Math. and Phys. Papers, Vol. 2, p. 307.

[3] Phil. Mag. (5), p. 153, 1876.

[4] Beibl., 7, p. 314, 1883.

[5] Pogg. Annal., 128, p. 202, 1886.

[6] Phil. Trans., 1883, p. 1.

[7] Wied. Annal., Vol. 31, p. 360, 1887.

deformations of the conductor, used his metals in thin deposits on glass. Three diamagnetic and three ferromagnetic metals were investigated, viz., Bi, Te, Sb and Ni, Co and Fe respectively. These metal films deposited on glass had two points of contact diametrically opposite and the plate was so arranged that it could be rotated about an axis normal to the plane of the glass. In this way the same points of contact could be used, but the direction of the flow of the current could be varied with respect to that of the magnetic field imposed upon it. His results are thus summed up: "Es nimmt also bei allen Metallen der Widerstand in der Richtung der Kraft linien zu; in der dazu senkrechten Richtung nimmt er nur in diamagnetischen Metallen zu; in magnetischen nimmt er ab." The hypothesis that change in resistance was due to deformations of the conductor, it seems, Goldhammer has pretty thoroughly disproved. Nickel, for instance, shortens its length for all field strengths applied longitudinally. Its resistance, according to Ohm's law, should decrease but instead we find it increasing when subjected to a longitudinal magnetic field.

Tomlinson concluded his study by saying that "the increase of resistance which is produced by magnetization is probably not merely due to the rotation of the molecules of the magnetized substance as molecules, but to the electrical currents which, according to Ampere's hypothesis, are constantly circulating around the molecules."

In 1900 Sir J. J. Thomson[1] explained this phenomenon on the corpuscular theory of electric conduction in metals. According to his theory, "the electric currents in the metal are carried by negatively charged corpuscles moving with a definite velocity under an applied E.M.F. These corpuscles are supposed to act as a perfect gas; consequently they have a mean free path and a mean velocity and exert a definite pressure. If the corpuscles are moving under an electric force and then a transverse magnetic force should be applied, the particles will move in cycloids, and the resistance will be increased. Similarly in a longitudinal field the electrons will describe spirals in their motion and again the resistance will be increased. It is to be noted that Van Everdingen[2] arrived at opposite conclusions regarding the transverse field effect in a theoretical paper which appeared not long after Thomson's. At the suggestion of Professor Thomson, Patterson[3] carried out a series of observations on the effect of a magnetic field on the electrical conductivity when applied transversely to the conductor. His experiments were performed on non-

[1] Rapports presentes au Congres International de Physique, 3, p. 138, Paris, 1900. Phil. Mag., p. 353, March, 1902.

[2] Communications from the Physical Laboratory of Leiden, No. 72.

[3] Phil. Mag., p. 643, June, 1902.

magnetic material such as German silver, copper, cadmium, zinc, gold, platinum, tin and carbon. In all of these conductors Patterson found that the transverse field tended to increase the resistivity unless in some metals which showed so little change that it was difficult to say just what did occur. Some of these same metal wires were also tested for the effect of a magnetic field applied in the direction in which the resistance was measured and here an increase was also found. His results are confirmatory of Thomson's theory so far as non-magnetic substances are concerned and seem to be a fairly satisfactory explanation. The theory, however, does not fit the results already cited for magnetic materials. Either the theory is not the proper explanation or else in the case of ferromagnetic conductors we have other factors in addition, which play important rôles. The latter seems plausible, as will be shown later, and possibly Van Everdingen's work may be utilized to fit the case of ferromagnetic substances.

Auerbach[1] has pointed out that in the Hall effect we have an E.M.F. developed normal to the lines of flow when the conductor is placed in a magnetic field and which ought to produce an apparent change in resistance. This is comparatively large in the ferromagnetic metals and may be one of the factors causing the difference in behavior of ferro and non-magnetic metals when placed in a transverse magnetic field.

We thus have many and varied reasons for this change in resistance, some of which are contradictory, but many are doubtless present and combine to give us the effects found.

Recently, I pointed out[2] that the majority of magnetic phenomena could be explained by assuming that the elementary magnet was an oblate spheroid about which negative electrons were revolving and that the orientation of such an elementary magnetic unit produced or at least influenced the magnetic phenomena which we know. If a ferromagnetic substance is made up of these oblate spheroids for the nuclei of the elementary magnets and the magnetic field gives them a definite orientation, what will be the effect on the electrical conductivity when the lines of flow are parallel to the equatorial planes of the spheroids and what will be the effect when the lines of flow are normal? In the thought that it might throw some light on this effect first discovered by Lord Kelvin, Mr. Paul Weeks, an advanced student in our department, has carried out the following experiments:

[1] Winkelmann's Handbuch der Physik, p. 458, Vol. 5, Pt. 2, 1908.

[2] PHYS. REV., abstract, Feb., 1911.

MR. WEEKS' EXPERIMENTS.

Wooden oblate spheroids, boiled in paraffine, were mounted, four on a wire, so that the equatorial planes contained the wires. The major axes were 1.74 cm. in length and the minor axes 0.82 cm. Sixteen such sets were completed and mounted so that the spheroids could be turned with the wires as axes. There were 64 spheroids and were grouped to form a cube as shown in Figs. 1 and 2. Fig. 1 is a vertical cross-section and Fig. 2 is a horizontal cross-section. These 64 spheroids were placed

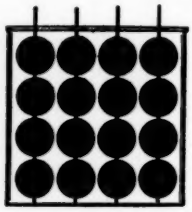

Fig. 1.

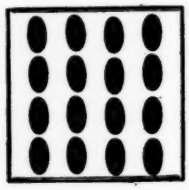

Fig. 2.

between two copper electrodes, 17×17 cm. square, and the whole inclosed in a paraffined wooden box with glass sides, as shown in Figs. 1 and 2. The box was 18 cm. deep and the horizontal cross-section, 17×17 cm.

Ordinary tap-water was poured into the box until the spheroids and electrodes were covered. The resistance was then measured by means of a Kohlrausch bridge when the spheroids were all turned with equatorial planes normal to the lines of flow, when parallel and for intermediate

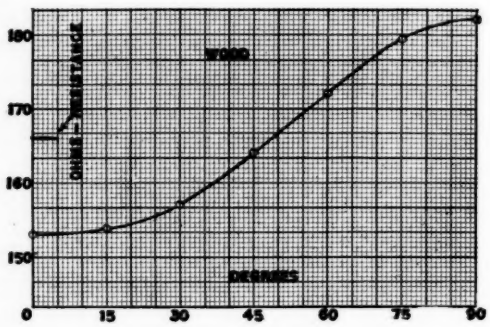

Fig. 3.

azimuths between 0° and 90°. The difference was very marked, the resistance being much greater when the equatorial planes were normal than when parallel to the direction of the current. In Fig. 3 is shown the way in which the resistance varied as the angle between the equatorial

planes and the current were varied from 0° to 90°. A similar experiment was also tried with the same sized spheroids made of type-metal in which the spheroids themselves were better conductors than the tap-water. Similar results were obtained here as in the case of the non-conducting spheroids, viz., an increased resistance when the spheroids were set with equatorial planes normal to the current. For the metal spheroids the total resistance was less than for the wooden ones. The results are shown in Fig. 4. Acidifying the tap-water with H_2SO_4, and increasing the

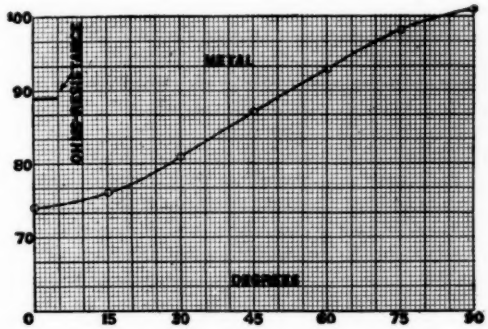

Fig. 4.

conductivity flattened the curves for the metal spheroids. If the tap-water had the same conductivity as the spheroids, orientation of the spheroids ought not to change the resistance.

DISCUSSION OF RESULTS.

In the curves of Figs. 3 and 4 it is of interest to note that they are the same type of curve which one obtains when plotting the lengths of the diameter of the spheroid about an axis lying in the equatorial plane as the diameter swings through 90° or the same type of curve which one obtains in plotting the area of the projection of the spheroid on a plane as the spheroid is turned through 90°. To put it another way, if one used as radii-vectors the values of the resistances obtained when the spheroids were turned in the different azimuths, from 0° to 360°, the curve traced out by the termini of the radii-vectors would be an ellipse. Goldhammer[1] plotted his results in this way for the different values of the resistance of a conductor when placed in a magnetic field and also found that an ellipse was the figure obtained when a line was drawn through the termini of the radii-vectors representing the resistances for the different angles between the direction of the magnetic field and the lines of flow of the current.

[1] *L. c.*

In a previous work[1] I have shown that to account for the changes in length of a ferromagnetic substance, when magnetized longitudinally, the orientation of oblate spheroids within the material would give the effects observed and that a shortening indicated that the obla te spheroids had their equatorial planes normal to the magnetic field. In iron and nickel this occurs in strong fields. Kelvin, Goldhammer, Tomlinson and Patterson worked with strong magnetic fields so that the oblate spheroids, if they exist, were oriented with their equatorial planes normal to the field. If resistance was measured normal to the field, then the current would flow parallel to the equatorial planes of the spheroids. For ferromagnetic substances this condition is the one for the decrease in resistance. It is also the condition found in the experiments reported here. Similarly, if the resistance is measured parallel to the field, there is an increase of resistance because the current flows normal to the equatorial planes. These experiments show increase in resistance when the current flowed normal to the equatorial planes. Thus for the metals which the theory of Thomson's did not cover, there is in these experiments a possible explanation. Cobalt lengthens for strong fields in which case it may be supposed that other factors, already mentioned, prevail. As was said above there can be little question but what we have a number of different factors combining to give us the effect described as change in resistance due to a magnetic field. It is a complicated phenomenon. In one metal one factor may predominate and in another some other factor may hold sway. In connection with the explanation offered in these experiments, it would be of great interest to measure the change in resistance of the Heusler alloys due to a magnetic field. They show increase in length for the Joule effect for all magnetic field strengths that have been studied.

The effect first found by Lord Kelvin is a comparatively small effect, hence strong magnetic fields are always used in studying it. If, however, the orientation of elementary magnets does play some part in this phenomenon, then we might expect a reverse effect for weak fields since the Joule effect shows a lengthening for weak fields and a shortening for strong in the case of iron and steel. The effect is doubtless too small to be detected in weak fields but nevertheless is worth trying for. This will be investigated in connection with a study of the Heusler alloys for change in resistance due to a magnetic field.

One point perhaps should be discussed: what is the cause of this change in resistance due to the orientation of the oblate spheroids within the conductor? If one maps the lines of flow about the spheroids, when the

[1] PHYS. REV., Vol. 34, p. 40, Jan., 1912.

equatorial planes are normal to the lines of flow and when they are parallel, it will be seen that the length of the path of flow is greater when the equatorial planes are normal to the direction of flow than when parallel. This amounts to increasing the length of the conductor and so augmenting the resistance, although the distance between the electrodes remains constant. This is shown in Figs. 5, 6, 7 and 8 where 5 and 6 are for the

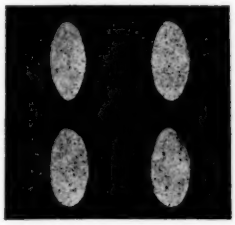

Fig. 5.

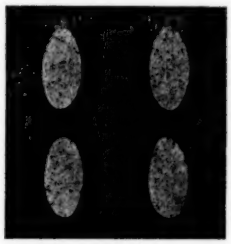

Fig. 6.

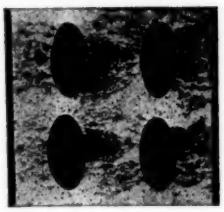

Fig. 7.

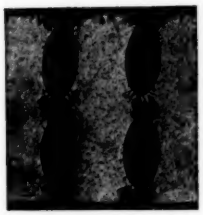

Fig. 8.

non-conducting oblate spheroids and 7 and 8 are for the conducting spheroids. The lines of flow were plotted by a method described by Hering.[1] In Figs. 5 and 6 the elliptical openings are cut in the conducting sheet and so are non-conducting, while in Figs. 7 and 8 zinc ellipses are laid on the conducting sheet and are better conductors than the sheet itself. There will also be a change in resistance due to change in cross-section of the electrolyte as the spheroids are rotated. This is also shown in Figs. 5, 6, 7 and 8.

The experiments as carried out were with the condition that the distance between centers of the spheroids remained constant. This is analogous to Goldhammer's experiments in which he used thin films plated on glass. The elementary magnets could not shift laterally. The resistance was also measured when the distance between the bounding surfaces was the same in both directions, the distance between the electrodes remaining as before. This did not seem to affect the general

[1] Hering's Essentials of Physics, p. 298.

results, observed when the centers were kept fixed. The heavy, horizontal lines in Figs. 3 and 4, marked by an arrow, indicate the resistance when the spheroids are turned in all possible directions. This would be analogous to the condition of a ferromagnetic substance in the virgin state.

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Dec., 1912.